ECONOMIC GEOLOGY

VOL. XXII AUGUST, 1927 NO. 5

OXIDATION PRODUCTS DERIVED FROM SPHALERITE AND GALENA.

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Definition of Terms.—By "oxidation products" of sphalerite and galena is meant the final products remaining in place of the sulphides after the cropping has been leached and no longer carries essential amounts of sulphates, carbonates, or other oxidized minerals of the original sulphides; the term, in other words, refers to the iron precipitates usually spoken of as limonite or limonitic jasper. Descriptions of the sulphates, carbonates, and other oxidized minerals of the sulphides is omitted because difficulty in their recognition is seldom experienced.

The terms "limonite" and "limonitic jasper," as here used, refer to the fine to medium grained reddish, brownish, or yellowish deposits from decomposing iron bearing minerals. Usually they consist of ferric oxide monohydrate (goethite) [1] with variable admixture of supergene silica; in some cases the goethite gives place to hematite, lepidocrocite, and certain ferric and ferric lead sulphates.

GENERAL STATEMENTS.

1. A point to note in considering the oxidation products of sphalerite and galena is that they ordinarily represent the end products of the massive or aggregated, sulphides; for sphalerite and galena usually occur massive, as contrasted with the copper and copper iron sulphides which more often occur disseminated. Previous papers have dealt largely with disseminated sulphides, and have touched upon the massive type only incidentally; this paper is the first to present the results of a comprehensive study of any of the massive sulphide types.

2. Unlike the limonites derived from iron and copper sulphides, those derived from sphalerite and galena are not usually the direct product of the attack upon the sulphides themselves; more often, as shown by field evidence, they result from attack of iron bearing solutions upon the secondary minerals, especially the carbonates. In other words, limonites derived from copper sulphides, by the

[1] E. Posnjak and H. E. Merwin, "The Hydrated Ferric Oxides," *Amer. Jour. Sci.*, 47, 311, 1919; also "The System Fe_2O_3-SO_3-H_2O," *Jour. Amer. Chem. Soc.*, 44, 1965, 1922.

same process, would not be limonites derived directly from chalcopyrite, bornite, or chalcocite, but would be those derived from azurite, malachite, or other oxidized copper minerals as these latter were attacked by iron-bearing solutions.

3. In the case of sphalerite and galena products, only indigenous limonites,—that is, those precipitated within the limits of the sulphide body,—are considered, as contrasted with both the indigenous and transported types for disseminated iron and copper sulphides. In the case of *massive* sphalerite and galena the iron often may migrate several centimeters within the limits of the oxidizing body before being precipitated, and still be subject to accurate interpretation as to origin; for in such cases the limonites from a given sulphide often maintain their distinctive characteristics, and they are properly termed indigenous so long as they are deposited within the limits of the particular sulphide nodule or mass from which they originated. On the other hand, iron transported more than several centimeters within the oxidizing sphalerite or galena body, or exported from the limits of that body and subsequently precipitated, usually is too contaminated with foreign substances for its history to be accurately read.

4. Experience in examining many deposits proves that leached croppings derived from sphalerite and galena commonly show less width and less continuous persistence along the strike at the surface, where exposed to ordinary erosion, than they do three to five feet lower down. Zinc and lead deposits frequently are lenticular, and it may be assumed that in some instances the accident of erosion has exposed the upper narrow portion of the lens. On the same basis, the accident of erosion ought nearly as often to expose the central wider portion of the lens, and the deposit in such case ought to decrease in size downward. Numerous examples illustrating both conditions have been found. But field evidence shows that after lenticularity has been taken fully into account in the case of developed properties where the shape and position of the lens with respect to the surface have been accurately determined, and particularly in cases where veins have a nearly uniform width and do not show notable lenticularity,

leached sphalerite and galena croppings exposed to the ordinary processes of weathering show contraction which often amounts to as much as one fourth to one half the volume. This does not mean that a given leached cropping invariably represents a larger body in depth; it does mean, however, that if the cropping shows promise, systematic stripping is warranted to determine whether there may not exist a larger body than is suggested by the exposed cropping alone. The risk of lenticularity of the deposit must still be taken.

5. The ability to interpret leached croppings, while constituting an important adjunct to the equipment of the geologist in judging a prospect, is an adjunct only, and cannot be expected to displace the established fundamentals, such as structural geology, that have been heretofore relied on in field work. For example, a district recently studied by the writers showed that although the leached croppings were an important aid in determining the value of untested ground—particularly in establishing the nature of the leached sulphides—nevertheless, because of the lenticular and erratic occurrence of the deposits along both strike and dip of the veins, the occasional exposed outcrops of leached sulphides were much less dependable guides to probable oreshoots than was the presence of small silicified spur veinlets branching from the main veins. Where such spurs coincided with limonitic croppings derived from the sulphide sought, the prospect was of course especially attractive. Thus, while the ability to interpret leached croppings equips the geologist with an instrument not previously available, and enables him to determine with greater assurance than was formerly possible the worth or hopelessness of a prospect, it is not a means to be used except in conjunction with all other geological aids that can be found in the district. This is especially true of vein and limestone replacement deposits, where the surface ordinarily furnishes a much smaller cross section of ore occurrence than does the surface over disseminated deposits in porphyry.

Acknowledgments are due H. W. Morse for submitting field observations regarding specific oxidation products, and for dis-

cussion and assistance in planning the paper; to George Tunell for detailed mineralogical determinations of numerous limonite specimens, and for suggestions regarding the chemistry of oxidation; to F. L. Ransome, Augustus Locke, and M. N. Short for criticism of the paper, and suggestions for its improvement after it was written; and to the owners and operators of the various mining properties visited, whose courtesies and coöperation made possible these investigations.

This paper, like the previous one on chalcopyrite oxidation products,[2] is intended for the use of the scout in the field.

DESCRIPTION OF THE OXIDATION PRODUCTS.

In Inert Gangues.

The type and principal kind of inert gangue is quartz.

Sphalerite and galena, oxidizing completely in such a gangue, not admixed with pyrite or other iron-bearing mineral, and not traversed during oxidation by iron-bearing surface waters, have not been found to leave limonite.

Neither has sphalerite been found to leave oxidized zinc minerals in such a gangue. In this respect, the leached croppings of sphalerite and pyrite resemble each other in that both usually leave clean cavities in the place of the former sulphide, so that without additional evidence in such case there is no way of telling from the leached cropping which of these two sulphides formerly occupied it.

In the case of galena, cerusite and to a lesser extent anglesite, is almost invariably present to some degree in the place of the former sulphide. Locally croppings have been found wholly leached of the oxidized lead minerals, but complete leaching is rare.

Inert gangues, therefore, when leached of sphalerite, ordinarily leave neither limonite nor oxidized zinc minerals; when leached of galena, no limonite is left, but oxidized lead minerals usually remain.

[2] Roland Blanchard and P. F. Boswell, "Notes on the Oxidation Products Derived from Chalcopyrite," ECON. GEOL., 20, 618, 1925.

In Environments of Moderately Slow Neutralizer.

The type and principal kind of moderately slow neutralizer is the feldspathic rock. The slightly silicified veins in the pre-Cambrian gneisses and schists of western Arizona and northwestern Mexico are good examples. In environments of this sort usually the best examples of oxidation products for both sphalerite and galena are found, and all the significant types thus far distinguished for any gangues are here well developed.

There have been distinguished three types for sphalerite and two for galena.

Oxidation Products of Sphalerite.

Coarse Cellular Boxwork.—This type, like that of the coarse cellular honeycomb of chalcopyrite derivation, is characterized by a siliceous boxwork with sharply defined, angular pattern. It contains numerous white to glassy quartz veinlets that show distinct parallelism of orientation, are invariably rigid, and often are continuous for several centimeters in a straight line past numerous cells. Rarely other veinlets of the white to glassy quartz cut across those showing parallel orientation. Veinlets vary in thickness from 0.1 mm. to 2.0 mm., and enclose between them individual cells varying in diameter from 0.2 mm. to 5.0 mm.

In studying both oxidized and primary sulphide specimens under the microscope, it was observed that no difference exists in composition, size, shape or pattern between the veinlets in oxidized and sulphide products, that the veinlets characteristically emanate from the quartz gangue that exists within or around the sulphide mass, and that they follow outward from such source along fracture planes. There consequently can be no doubt as to their hypogene origin.

It was further observed that as oxidation of the sulphide mass proceeds, the veinlets gradually advance their front and "eat" their way into the less coarsely fractured portions of the sulphide mass. Often these extensions persist along fracture planes and maintain in the structure parallel orientation of the cell walls. More frequently they branch around the sulphide grains in irreg-

ular pattern, and in rare instances cut across individual grains, until a connected webwork extends throughout the sulphide mass with only unoxidized or partly oxidized sulphide residuals filling the intervening spaces. These extensions of the white to glassy veinlets consist, not of pure silica, but of limonitic jasper, and are clearly supergene. (See Fig. 1.)

FIG. 1. Sphalerite showing beginning of oxidation. Dark portions: sphalerite. Broad, white bands: hypogene quartz veinlets. Thin, irregular white stringers cutting sulphide lenses: limonitic jasper veinlets "eating" their way into the sphalerite mass around individual sulphide grains. × 1½. Golconda Mine, Chloride, Arizona.

As oxidation proceeds still farther, the sulphide residuals become oxidized, leaving behind the cellular boxwork described. To this extent the processes of oxidation and formation of the boxwork do not differ from those in the coarse cellular boxwork of chalcopyrite derivation described in the previous paper. It is the physical characteristics of the limonitic jasper of the boxwork that differentiates the two types.

In the cellular honeycomb derived from sphalerite the limonitic

jasper forms a more continuous webwork between the hypogene quartz veinlets, there is greater uniformity of cell size, individual cell walls are more firmly joined to the walls of other cells, and there exists greater variety of parallel cell orientation than in the case of the chalcopyrite product. Not infrequently definite series of cells form parallel cross structures between the hypogene silica

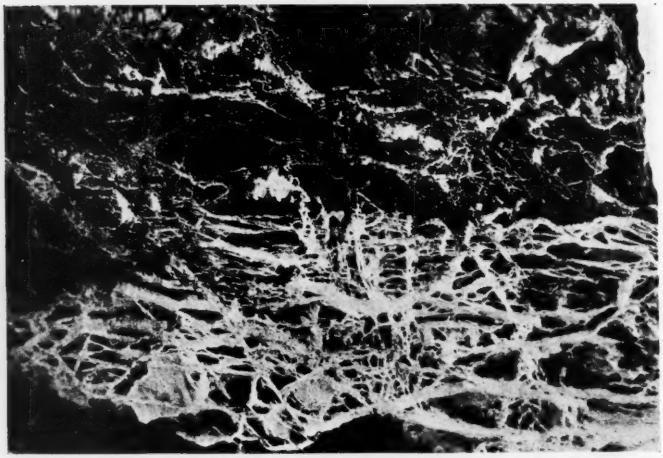

FIG. 2. Coarse cellular boxwork derived from sphalerite. White bands: hypogene quartz veinlets. Dark cellular structure: limonitic jasper. Note roughly parallel cell structures of the limonitic jasper, with well joined cell walls. × 1½. Golconda Mine, Chloride, Arizona.

veinlets. No firm rule can be laid down in this respect in contrasting the products derived from chalcopyrite and sphalerite, and for particular specimens there may be exceptions to the description just given; but the writers' observation in many districts is that parallelism of cell structure in the limonitic jasper crosswise of the main structure is from two to ten times as pronounced where the product is derived from sphalerite than where it is derived from chalcopyrite.

The most outstanding characteristics, however, of the limonitic jasper derived from sphalerite is the thinness of the cell walls (ordinarily ranging from less than .01 mm. to .2 mm.) and their flaky, shriveled appearance. This shriveled appearance combined with the thinness of the wall, has not been observed as common to limonites of other than sphalerite derivation. Unlike the chal-

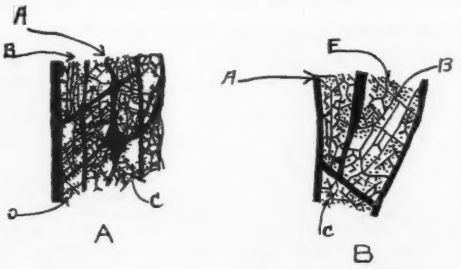

FIG. 3. A sketch showing characteristic coarse cellular boxwork of sphalerite derivation. Spruce Mountain, Nevada. × 2. *A*, hypogene quartz veinlet; *B*, parallel cell walls of supergene limonitic jasper; *C*, limonitic rosettes; *D*, sandy grains of limonite on cell wall. Note well connected cell walls and nearly empty cells; also parallel cell walls of limonitic jasper crosswise of the main structure.

B. Sketch showing characteristic coarse cellular boxwork of chalcopyrite derivation Bagdad, Arizona. × 2. *A*, hypogene quartz veinlet; *B*, parallel cell walls of supergene limonitic jasper; *C*, limonitic rosettes; *E*, pulverulent, slightly coalesced limonitic grains. Note broken cell structure, scarcity of cross structure and limonitic rosettes, and local abundance of pulverulent limonite in cell cavities. Absence of pulverulent limonite in some cells due to admixed pyrite.

copyrite product, the cells between walls likewise carry almost no limonite. Such limonite as is present is not the pulverulent, slightly coalesced type common to the chalcopyrite products, but is more sandy in appearance, and the individual grains are thinly scattered, rarely covering as much as one tenth the cell wall surface. In addition to the thinly scattered sandy grains, the cell walls often contain small limonite rosettes, 0.1 mm. to 0.5 mm. in diameter, of irregular size and in irregular aggregates, that

project outward from the cell walls. These, though not absent, are much rarer in limonitic jasper of chalcopyrite origin.

Orientation of cell structure, especially of the limonitic jasper, though parallel in a general way, is not rigidly so, and the continuous walls usually show slight pinches and swells throughout their lengths. But in contrast to the heterogeneous cell orientation present in most of the honeycomb mass, the series of cells connected in straight lines show distinct parallelism.

The limonitic jasper of sphalerite derivation sometimes, though not always, carries small amounts of calamine. This product, when present, aids in establishing the origin of the limonite, but independently of the physical characteristics above described does not establish the full origin; for calamine may be present in limonites of other origin, particularly in those of galena which carried a very small amount of sphalerite.

Summarizing: the thin, flaky, shriveled appearance of the cell walls in limonitic jasper derived from sphalerite. their well joined cell wall structure, and the scattered, minute sandy grains and occasional aggregates of small limonite rosettes projecting from the cell wall surfaces, constitute the most outstanding and most readily recognized characteristics that distinguish this product from limonitic jasper derived from other sulphides.

Fine Cellular Boxwork.—This type grades into the coarse cellular boxwork, and is usually present in varying amounts in that product. It differs from the coarse type in never having the larger size cells (cell diameters in this type rarely exceed 0.5 mm.), in containing few or none of the hypogene quartz veinlets, and in possessing less rigidity of structure. It is comparable to the fine cellular limonite of chalcopyrite origin, but differs from that product in having more firmly joined cell walls, and in the cell walls being made up of the very thin, shriveled limonitic jasper with only scattered sandy limonite grains or small limonite rosettes projecting from the cell walls. Unlike the fine cellular product of chalcopyrite derivation, the boxwork rarely crumbles into a pulverulent product when jarred or lightly touched. When firmly crushed between the fingers, it collapses to a fine, dry flaky

product very similar to the crushed iron rust blisters of mine rails. Its distinguishing characteristics that can be most easily recognized in the hand specimen are, as in the case of its coarser type, the well joined walls of thin, shriveled limonitic jasper with their essentially empty cells but with scattered sandy grains or rosette aggregates of limonite projecting from the cell wall surfaces.

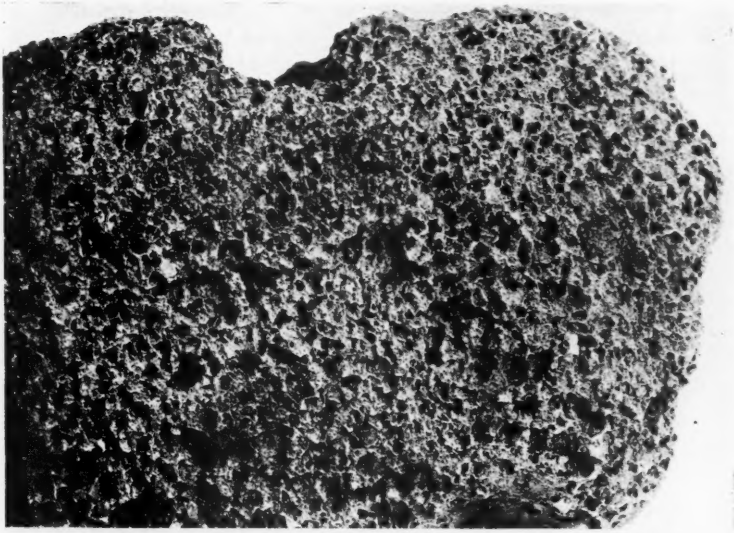

FIG. 4. Cellular sponge derived from sphalerite. See text for description. Note particularly the nearly empty cells with thinly scattered limonitic grains on cell wall surfaces. × 1½. Empire Zinc Mine, Hanover, New Mexico.

Cellular Sponge.—This type differs from the two above described in having no sharply angular boxwork pattern, in possessing characteristically thicker and slightly more rounded cell walls, and in being so rigid that it will resist a light blow without disintegrating. Cells are of medium size, ordinarily ranging in

diameter from 0.2 mm. to 2.0 mm. Cell wall thicknesses vary, but for the same size cell are usually from two to five times as thick as in the boxwork types. In texture and general appearance, the cellular mass resembles closely a rubber bath-sponge. (Fig. 4.)

The limonitic jasper of the cellular mass often contains as much as 25 to 50 per cent. supergene silica. Very fine, crystalline calamine, too small usually to be recognized by the unaided eye, also is commonly present in this type. In well leached specimens, however, it rarely constitutes 5 per cent. of the volume. The abundance of these silicates imparts to the sponge structure its high rigidity.

The cellular sponge possesses a dry, crisp appearance, and the cell walls carry the thinly scattered, sandy limonitic grains and occasional minute rosette projections common to the boxwork types; but the cell walls, because of their greater thickness, do not have the pronounced flaky, shriveled appearance of the boxwork types.

This cellular sponge is the product most likely to be confused with the fine-celled limonitic sponge of massive pyrite origin described in the previous paper;[3] and like that sponge it is most commonly found where the sulphide was traversed during oxidation by solutions of moderately rapid neutralizer, such as $CaCO_3$. It may be distinguished from the massive pyrite product by:

1. The cells, while more rounded than those of the boxwork types, nevertheless show much greater angularity than those of pyrite derivation. (Compare Fig. 4 with Fig. A, Plate I of the chalcopyrite paper.)

2. Cells occur uniformly throughout the mass, instead of erratically.

3. Cell walls contain appreciable silica in the form of limonitic jasper and often carry minute crystals of calamine.

4. Cell-wall thicknesses, while variable, show much less abrupt variation over a given area than do those of the pyrite product.

5. There are rarely if ever present the thin, smeary crusts and

[3] ECON. GEOL., 20, 634, 1925.

"painted" films of black or iridescent limonite common in the pyrite product.

Oxidation Products of Galena.

Galena, protected by its anglesite coating during oxidation, usually remains to some extent residual in the cropping. Where the galena is wholly leached, varying amounts of anglesite and especially cerusite usually remain to guide interpretation.

But full dependence upon the presence of galena or oxidized lead minerals in the cropping cannot be had, since small amounts of these may persist in leached croppings derived from other sulphides that carried only unimportant amounts of lead. Furthermore, oxidized lead minerals sometimes are completely leached from croppings that formerly carried them abundantly. If the cropping derived from galena is to be correctly read, the physical characteristics of the limonites themselves must be depended on for interpretation.

Limonites derived from galena have three physical properties that aid in establishing their origin.

1. *"Cleavage" Boxwork.*—Running through the galena limonites there is commonly present a series of straight, very thin plates of limonitic jasper, unvarying in their parallelism, somewhat resembling the structure that could be imagined for mica schist if every fifth or sixth plate were in its original position, with intervening plates removed. In the galena limonites, the plates or cell walls of the boxwork vary in thickness from 0.005 mm. to 0.05 mm.; they are among the thinnest walls ordinarily found in cellular limonites. Frequently cross structures of parallel plates run at right angles to those forming the main structure, and where this occurs, a cubic boxwork results; but as a rule the structure is well developed in one direction only. The cubic boxwork has been traced in many specimens directly into the cleavage of the galena, and the size of the boxwork in a given case depends upon the size of the more readily cleavable faces of the original sulphide. Usually the diameter of the "boxes," or the distance between parallel plates, does not exceed 1.0 mm. In more coarsely crystalline galena the structure, though present, is less well preserved in the oxidized products.

Since galena rarely has been observed in the field going to limonite without having first passed through the anglesite and usually through the cerusite stage, it is a matter for surprise that the cleavage structure of the original galena should be preserved in the final limonite product. The field evidence is that, although by no means prominent, this residual cleavage structure does remain to some extent in every cropping examined by the writers, embracing those as widely separated geographically and subject to as varied climatic conditions as exist between northern British Columbia and central Mexico. The reader is warned, however, that this structure is not as obvious as the descriptions might imply. In many places it is obscured or covered by the superposed crusts described below. Often areas only two to three centimeters square do not show the structure, but rarely have the writers examined a specimen five to six centimeters square that did not reveal it to some degree. The "cleavage" boxwork may be emphasized in the hand specimen by throwing a strong light obliquely upon the limonite so as to produce shading of the cellular mass.

2. *Partially-Sintered Crusts.*—The thin walls of the "cleavage" boxwork, once formed, commonly persist through later stages of leaching, but nearly always there are superposed upon them crusts of another limonite that may completely obscure the original boxwork except on cross-sectional breaks. These younger crusts have a partially-sintered appearance, like the surface of dead-burned magnesite brick but slightly rougher. They are from two to ten times as thick as the "cleavage" boxwork walls, and often extend out into the cell sufficiently to reduce the original cell diameter by one half. Locally the crusts may consist of tiny rosettes, like those of limonite derived from sphalerite, but in the case of lead these are usually much smaller, have the partially-sintered rather than the dry, shriveled appearance and therefore are not easily confused with the sphalerite product. These crusts and rosettes often carry grains of cerusite, and this furnishes an additional clue in establishing the limonite's origin. Where the cerusite is lacking, the partially sintered appearance,

with the occasional thin "cleavage" boxwork walls persisting through it, alone may serve to establish its derivation. Only rarely do these partially sintered crusts have embedded in them the sandy limonite grains common to sphalerite types.

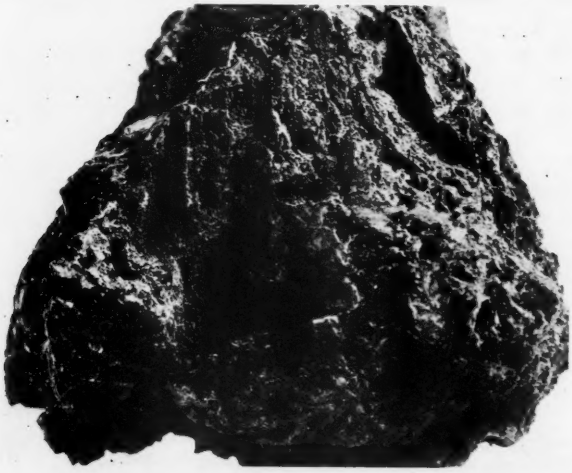

FIG. 5. "Cleavage" boxwork derived from galena. Note rigid parallelism of cell walls, and thick coating of partially-sintered limonitic crusts. Note particularly at bottom the more rounded, botryoidal limonitic crusts derived from pyrite. $\times 3$. Ruby Hill, Eureka, Nevada.

The "cleavage" boxwork, with its crusts of partially sintered limonite, usually is so fine-celled that its distinguishing characteristics are not easily discernible in the hand specimen. But the writers have seen no specimen with structure so fine that the "cleavage" boxwork or the partially sintered crusts and rosettes, or both, could not be distinguished with the hand lens.

3. *Color.*—The "cleavage" boxwork type of limonite derived from galena possesses also a distinguishing ochreous-orange color. This color is nearly universal on freshly broken surfaces, though on weathered surfaces the color ranges from ochreous-orange

through seal brown to dark chocolate. It is distinguishable in the hand specimen from the characteristic deep ochreous product in the fine cellular limonite of chalcopyrite origin by its deeper orange tint, and a certain velvety, rather than pulverulent, slightly coalesced appearance. When once clearly recognized, it is not likely to be confused with the chalcopyrite product.

The ochreous-orange color alone does not distinguish it from certain types of similarly colored limonites of bornite derivation: this criterion must be used in connection with other physical properties, described below.

It should be remembered in this connection that limonite color is dependent upon grain size, state of aggregation, and often upon the preponderant mineral. The grain size and state of aggregation in turn are dependent upon variations in acidity of the iron depositing solutions, rapidity of neutralization, effects of adsorption (in kaolinic gangues), and on various other factors. Any approach to universality in limonite color over extensive areas is therefore not to be expected on hypothetical grounds. Nevertheless, field evidence shows that in most cases, regardless of geographical distribution or climatic conditions, the fine cellular limonite of chalcopyrite derivation usually has the characteristic deep ochreous color; most limonites of chalcocite derivation have a maroon color, though in some districts a seal brown to Bismarck brown is more characteristic, and in certain districts a yellow-ochreous color is common; those of bornite derivation frequently, though by no means as commonly, have a distinctive ochreous-orange color; those of galena derivation, more universally than any of the types mentioned, have the ochreous-orange color on freshly broken surfaces.[4]

[4] Tunell has established through extensive microscopic work that in the case of chalcocite limonites the maroon or reddish color is due to a high hematite content in the "limonite"; the seal brown or Bismarck brown color to predominant goethite; the yellow-ochreous color to predominant jarosite. This suggests that the deep ochreous limonite of chalcopyrite derivation may be largely goethite, and that the ochreous-orange products of galena, and to a lesser extent of bornite, may be largely goethite but with slightly more hematite than possessed by the chalcopyrite product. The mineralogical determinations of the galena, sphalerite, and bornite limonites made by Tunell in connection with this paper bear out these assumptions, and show

Confusion with Limonites Derived from Bornite.

As previously stated, the ochreous-orange limonite derived from bornite cannot be distinguished, on the basis of color, from that derived from galena. It may be distinguished by (1) Lack of the "cleavage" boxwork; the cell walls being either indefinitely parallel or showing no parallelism at all. (2) The cell walls are rarely completely formed on all sides of the cell, and where complete they join at all angles the walls of surrounding cells. (3) The cell walls are usually distinctly thicker than those of the "cleavage" boxwork. (4) Cell walls and intercellular spaces in the case of bornite, instead of being coated and largely filled with partially sintered crusts and rosettes, are rarely as much as half filled, and the material contained in the cell consists of pulverulent limonite with very slight coalescence of particles.

Confusion with Limonite Derived from Siderite.

The "cleavage" boxwork type of limonite is sometimes confused with limonite derived from siderite or other ferruginous carbonate, for these latter products also often show the thin, rigidly parallel "mica plate" structure running through them. But in the case of siderite and other ferruginous carbonates, the rhombohedral structure of these plates with their frequent, slightly curved cleavage faces, serves to differentiate this product from the cubical boxwork of galena derivation. Furthermore, the "plates" are not coated with the partially sintered crusts of limonite, but are embedded in the highly porous, fluffy product characteristic of limonite precipitated by rapid neutralizer.

Confusion with Limonite Derived from Magnetite.

The "cleavage" boxwork type of limonite is likewise sometimes confused with limonite derived from magnetite. Where the magnetite crystallized out as cubes, the "cleavage" boxwork is sometimes preserved in this limonite, as at Morenci. Further-

further that in the case of the galena limonites plumbojarosite may be less common than has been generally supposed. Work on a much larger number of specimens, however, is needed before these conclusions may be accepted as established.

more, the limonite derived from magnetite in some cases, though not consistently, has the ochreous-orange color, and when derived from fine, granular magnetite it often has the velvety appearance in the hand specimen that was mentioned above as present in certain galena oxidation products. Usually, however, the magnetite limonites possess a distinctive irregular cellular pattern, difficult to describe but not readily confused with other types when once it has been clearly recognized. In no instance, have the writers observed the partially sintered limonitic crusts in the magnetite product, and their absence in this type of limonite furnishes reasonable assurance that it is not of galena origin.

Confusion of the galena limonites with those derived from magnetite is never likely to occur except in the hand specimen; for magnetite oxidizes to limonite very slowly, and in the field the writers have never seen such limonite penetrate the magnetite more than eight inches except along fractures. At Morenci, at Hanover, New Mexico, and at Iron Springs, Utah, where in the writers' experience are found the best examples of limonite derived from magnetite, the magnetite is many times more abundant than its limonite derivative, and invariably grades within a few inches into the latter. Except locally, the magnetite shows no supergene alteration that can be detected with the hand lens.

Ragged Cellular Type.—The "cleavage" boxwork type of limonite is the only one thus far found as a dependable guide to galena over extensive areas.

Another type occurs in numerous districts, and in particular districts is often significant. It consists of a honeycomb, more coarsely cellular than the cleavage boxwork structure, with cells less regularly parallel and more ragged in appearance, with the partially sintered limonitic crusts poorly developed, and, rarely, with cerusite or other lead minerals remaining.

This type has been observed only where the galena carried an important admixture of pyrite. With increase of the pyrite content, the physical properties characteristic of the "cleavage" boxwork type become more and more indefinite. There is a gradation into a cellular mass with thick walls and rounded open-

ings, the latter coated with smeary crusts and "painted" films of black or iridescent limonite, such as is described in the earlier paper as one of the types characteristic of massive pyrite oxidation.[5]

A feature that, in conjunction with other physical properties helps to distinguish this type is the characteristic ochreous-orange color that grades through seal brown to dark chocolate. All these colors usually are present on freshly broken surfaces, with the darker colors predominating as the pyrite content of the original sulphide increases. With pronounced predominance of pyrite, the color often changes to a dull reddish brown, and contains veinlets and thick crusts of a hard, sub-metallic limonite with numerous shrinkage cracks. Only the intermittent persistence through this ragged structure of the "cleavage" boxwork and the partially-sintered limonitic crusts, permits classification of the material as a limonite derived in part from galena. Quantitative estimate of the former galena content in the cropping is not possible, but if the cellular structure reveals the products proved characteristic of galena oxidation, assurance may be felt that the cropping formerly carried galena even though lead minerals no longer remain in the cropping and even though it is clear that the predominating sulphide was pyrite.

Interpretation of this type of limonite is never wholly satisfactory because the amount of lead formerly in the cropping cannot be estimated. The product merely shows that lead in some indefinite amount formerly was present.

Theoretically, pure sphalerite and galena, oxidizing in an environment of moderately slow neutralizer, and not traversed during oxidation by iron-bearing waters, should not leave indigenous limonite any more than where they oxidize in inert gangues. Evidence from many districts shows, however, that in the feldspathic gangues these sulphides usually do leave their characteristic limonites. Suggested explanations are, (1) in feldspathic gangues these sulphides carry admixed pyrite much more commonly than they do in quartz gangues; (2) in the case of sphalerite there

[5] ECON. GEOL., 20, 634, 1925.

usually is some isomorphous iron; (3) during oxidation, iron-bearing surface waters may come more often and more continuously in contact with the oxidizing sulphides because the gangue less often outcrops above the surface; or, finally, two or more of these conditions may prevail and a source of iron frequently absent in the inert gangues, be therefore available for the limonite-making reactions.

Irrespective of the particular cause or causes, the fact is well established from field evidence that indigenous limonite after sphalerite and galena is common in environments of moderately slow neutralizer, and it seems probable that the gangue played at least a small part in the limonite's precipitation.[6]

In Environments of Rapid Neutralizers.

The type and principal kind of rapid neutralizer is calcite, usually as limestone.

Insofar as the reactive gangue (such as limestone) is prevented from taking part importantly in the limonite-making reactions, the three types of limonite for sphalerite and the two for galena, above described, form as readily in limestone as in gangues of moderately slow neutralizer. Unfortunately, in a limestone gangue, limonites commonly are precipitated by the rapid neutralizer, $CaCO_3$. Consequently the limonite precipitates in such gangues nearly always have their significant characteristics modified or partly obscured. Strong neutralizer in the gangue or in solution interferes with the formation of the significant limonite types before their distinguishing characteristics are well developed, and such characteristics as are developed usually are masked to a greater or less extent by the fine, fluffy type of pulverulent limonite described in the previous paper as distinctive of no par-

[6] Private communication from George Tunell, 9/21/26: "I notice in this paper you attribute a certain amount of indigenous limonite to neutralization by surrounding gangue of moderate neutralizing power. I was forced to this conclusion also in the work at Morenci, Bingham and Tyrone (in investigating the disseminated chalcocite-enriched ores in porphyry). In the case of the porphyry copper ores, however, I think it likely that the reactions between solutions and sulphides are more rapid than those between gangue and solutions."

ticular derivation, but characteristic of limonite from any source where the iron-bearing solution came in contact with rapid neutralizer. In the case of sphalerite there is the further tendency for the flaky, shriveled walls of the coarse and fine cellular boxwork types to thicken, and for these types to approach and grade into the cellular sponge type.

Nevertheless, in most limestone deposits examined the significant features for both sphalerite and galena usually are discernible if carefully looked for beneath the fluffy limonite particles. These two sulphides rarely occur disseminated in limestone; usually they occur in nodules several centimeters in diameter, or as massive bodies of greater dimensions; and in the larger nodules the inner portion of the mass often reveals one of the characteristic limonite types even though this was masked near the outer surface. To put it another way—the effects of rapid neutralizer, even in limestone areas, do not ordinarily penetrate to the center of an oxidizing sphalerite or galena nodule several centimeters in diameter sufficiently to obliterate wholly the significant limonites derived from those sulphides. Exceptions of course exist.

The impression should not be gained, however, that it is easy to interpret limonites precipitated in gangues of rapid neutralizer. Distinctions between oxidation products left by the different sulphides and by other iron-yielding minerals are difficult enough to determine when the products are the result of air-water-acid processes alone; when complicated by the addition of foreign substances, or masked by precipitates of uncertain origin—such as the fluffy type precipitated by rapid neutralizer—interpretation of the final products is far from easy, and the same assurance never can attach to the interpretation as in the case of products oxidized normally in environments of moderately slow neutralizer. Close observation, and experience in relating the various products to their known sources in many districts and under varied oxidizing conditions, alone enables the scout to state definitely that any of the significant limonite types, when partly masked, was derived from sphalerite, galena, chalcopyrite, or other specific mineral, and cases will be met with in which even the person experienced in

interpreting leached croppings must admit a large degree of doubt. The definiteness of his conclusion, as regards the original volume of a particular sulphide, varies with the percentage of limonite in the cropping that can be definitely related to that sulphide. In other words, if, in a limestone cropping that shows much of the fluffy limonite, a third of the total limonite can be definitely related to galena and no other significant limonite types are recognized, the probability is good that more than a third was derived from galena; but the scout is not justified in stating this as a fact.

In particular districts local limonite types may express themselves, and these, if proved characteristic of a given mineral, will serve as a guide even though they may not have universal application. For example, in the limestone areas of the Patagonia, Arizona district limonites derived from sphalerite usually express themselves as the cellular sponge type. They are prominent in outcrops over most of the zinc deposits, and are readily distinguishable from the limonites derived from associated chalcopyrite and pyrite. In these same limestone areas, the limonite derived from lead minerals shows only weak development of the "cleavage" boxwork, the partially sintered limonitic crusts, and the ragged cellular structure. It does, however, possess a certain semi-granular, semi-pulverulent, velvety texture with the characteristic ochreous-orange to chocolate color, and under the hand lens reveals a very fine though somewhat indefinite cellular pattern. These properties distinguish it from the fluffy limonite precipitated by strong neutralizer, and in this district it has proved a dependable guide to prospecting for lead not only in the limestone but also in the kaolinized and alunitized rhyolite.

Mixed Sulphides.

In the case of mixed sulphides, where different sulphides often oxidize side by side at the same time, it is reasonable to assume that the respective oxidation products will intermingle and prevent intelligent interpretation of the final product.

To some extent this is true. It is especially true where pyrite is admixed importantly with other sulphides. But where pyrite

is present in only small amount, and the sulphide body is some galena-sphalerite-chalcopyrite combination (the most common mixtures, excluding pyrite, ordinarily found in primary lead and zinc deposits), the field evidence is that where the respective sulphide masses in the body are one half centimeter or more in length, intermixing of the oxidation products except along the edges is slight, and limonites characteristic of any particular sulphide are found indigenous to the areas originally containing such sulphide. As the pyrite content increases, the tendency likewise increases for the various oxidation products to "run together"; until, in cases where pyrite predominates, only occasional small areas may remain to show derivation from sulphides other than pyrite, and no basis will exist for estimating quantitatively the amount of a given sulphide in the original body.

The important point is that where in mixed sulphides the pyrite content is low—ordinarily well below one fourth the total volume—and the other sulphides consist of galena-sphalerite-chalcopyrite combinations, the leached cropping usually contains evidence from which the former content of the respective sulphides, on a quantitative basis, is to some degree inferrable.

In certain deposits, particularly those of lead, the oxidized products have associated with them various minerals which prove that the primary ore carried important admixtures other than sphalerite, chalcopyrite, or pyrite. The frequent association of wulfenite and vanadinite with the oxidized lead deposits of the West leaves no doubt about primary molybdenum and vanadium compounds having existed and oxidized contemporaneously with the lead minerals. In certain deposits molybdenite has been observed thus oxidizing side by side with galena. In other places arsenical compounds have left an apple green stain (presumably ferrous arsenate) on the lead limonites, suggesting that arsenic in some form was associated with the primary lead minerals. Picked specimens of such croppings at Spruce Mountain, Nevada, show as much as 13 per cent. As; those from Triunfo, Lower California, nearly half this amount.

Many of the deposits showing the above named oxidation

minerals have not been explored to the primary zone. Except for certain of the deposits containing wulfenite it therefore is not known in most cases whether these associated minerals were derived from their own homogeneous primary sulphides, or from lead-arsenic, lead-molybdenum-vanadium, or other complex sulphide forms. Their derivation, and frequent marooning of some of them in the otherwise leached croppings, present special problems like that of the large masses of gypsum and native sulphur associated with the oxidized lead orebodies at Ahumada, and call for further study before their significance in terms of ore becomes fully apparent. It suffices here to state that where these minerals are present in large amount in the croppings it often is difficult to recognize the characteristic lead limonite types, even though oxidized lead minerals are known to lie beneath. In some cases, at least, this probably is due to the fact that the primary lead ore was a complex sulphide instead of galena. On the other hand, where the associated oxidized minerals are present only in small amount in the croppings over oxidized lead orebodies, the specific lead limonite types already discussed usually are not greatly obscured. In this paper no attempt is made to discuss interpretation of croppings of the complex sulphides, nor of mixed sulphides other than the galena-sphalerite-chalcopyrite-pyrite combinations.

Summarizing, limonite types described in this paper are peculiar to sphalerite and galena oxidation; they have not been found as derivatives from other sulphides, and have been found dependable guides in the various districts visited. Superficially they resemble certain chalcopyrite and bornite products, but the distinguishing features described, when once clearly visualized, serve to differentiate them from the products of all other sulphides and of all other iron-yielding minerals whose oxidation the writers have studied.

CHEMICAL CONSIDERATIONS.

The chemistry involved in the oxidation of sphalerite and galena is simpler than that involved in the oxidation of the copper and copper-iron sulphides. Both sphalerite and galena contain

enough sulphur to dissolve completely in solution; and since neither, in its pure state, contains iron, and neither requires attack by iron-bearing solutions for its oxidation, it follows that no limonite need result.

The copper and copper-iron sulphides, on the other hand, either contain iron indigenous to the sulphide, or, as in the case of chalcocite, oxidize and are removed in solution by imported ferric sulphate. A source of iron available for limonite-making reactions therefore is present when the copper and copper-iron sulphides go into solution. (Covellite is an exception to this general statement.) Since they do not contain enough sulphur to dissolve completely both the copper and iron content, and since the copper is more soluble than the iron, it is to be expected that some of the iron, in the form of limonite, will remain.

Furthermore, since in the case of the copper and copper-iron sulphides, iron-bearing solutions are involved in the oxidation, limonite is a direct product of the oxidation of the sulphides themselves. In the case of sphalerite and galena, where iron-bearing solutions are not necessarily involved in the oxidation, limonite need not be the direct product of the oxidation of the sulphides; it may be and usually is, as suggested by field evidence, a product of the attack upon and oxidation of the zinc and lead carbonates or other oxidized equivalents by iron-bearing solutions; and therefore may be an indirect, not a direct, product of the oxidation of the sulphide.

Therefore, while the chemistry of the oxidation of sphalerite and galena is simpler than that of the copper and copper-iron sulphides, the final formation of limonite resulting from such oxidation may be much less simple than that of the latter sulphides.

Limonites derived from the oxidation of the copper and copper-iron sulphides, being direct products of such oxidation, might properly be expected to retain some of the structural characteristics of the sulphide body, such as the cellular boxworks patterned after the original structure of the sulphide mass. Limonites derived from the oxidation of sphalerite and galena, being com-

monly products of the oxidation of secondary minerals such as carbonates (as shown by field evidence), and therefore indirect, would be expected less often to preserve the original structure of the sulphide bodies. That they do often preserve it, as, for example, in the case of the "cleavage" boxwork of the galena product, is a matter that might properly be doubted, were it not for the field evidence which establishes it as a fact.

Oxidation by Air-Water Processes.

The two reactions,

$$ZnS + 2O_2 = ZnSO_4,$$
$$PbS + 2O_2 = PbSO_4,$$

represent the simplest equations in the oxidation of sphalerite and galena. According to these equations, no reactive agent except O_2 from the air is needed to oxidize either sulphide to its sulphate equivalent, though there is no positive evidence that catalysis may not play a part.

If water circulates through the area, the sulphate may in time be removed. At ordinary temperatures and pressures, zinc sulphate is soluble to the extent of 43,000 mg. per liter of water, and a mole could be removed when 2/5 liter of water had passed over the containing area. Lead sulphate is soluble to the extent of 42 mg. per liter of water, and a mole of it could be removed when 72,143 liters of water had passed over the containing area. Being nearly insoluble, the lead sulphate would remain in the cropping much longer than the zinc sulphate.

On this basis, it would be expected that in a wholly inert environment, oxidation of both sphalerite and galena would proceed by air oxidation; that most or all of the zinc sulphate would be removed in solution and leave no trace of itself behind if waters circulated through the oxidized area; that the lead sulphate, under the same conditions, would be removed very slowly, and usually would remain in appreciable amounts in the cropping, especially if oxidation of the galena had been recent; but that in neither case would limonite be left in the cropping to mark the place of the former sulphide.

With incoming CO_2 in solution, both the zinc and lead sulphates would in time be converted into carbonates. At ordinary temperatures and pressures, zinc carbonate is soluble in water to the extent of 100 mg. per liter; lead carbonate to the extent of 3 mg. per liter of water. If the water is saturated with CO_2, the solubilities in both cases are increased about five fold.

Hence it is evident that in an inert environment traversed only by water carrying CO_2 in solution, both the zinc and lead sulphates would in time be converted to carbonates; that the waters might readily dissolve and carry off the zinc carbonate in solution; that they would much less readily dissolve and carry off the lead carbonate in solution, but, given time, might remove it also; but that in neither case would limonite be left to mark the place of the former sulphide.

In other words, in an inert environment traversed only by surface waters that carried no iron-bearing minerals and no other reactive agents except CO_2, sphalerite would be expected to oxidize and be removed without leaving behind evidences in the form of secondary minerals. Galena would be expected to oxidize more slowly, and ordinarily to leave behind much of its lead in the cropping either as sulphate or carbonate, unless leaching had been vigorous and had been in process a very much longer time than in the case of corresponding sphalerite. But that in neither case would limonite be left in the place of the sulphide or its oxidized minerals.

This checks with conditions actually found in the field, and explains why lead minerals usually are not wholly leached from an inert environment while zinc minerals usually are. It likewise explains why limonite usually is absent in such a cropping, since no iron-bearing solutions are at any time necessarily involved in the oxidation and removal of the zinc and lead minerals.

A further condition to note is that galena first oxidizes to sulphate; that this nearly insoluble mineral ordinarily coats and encloses the oxidizing galena from which it was derived; and that this nearly insoluble coating tends to keep further oxygen from reaching the galena. This explains why so frequently unoxidized

galena residuals are found in a lead cropping that has been undergoing oxidation for a long time.

The principal kind of inert environment usually is quartz, but limestone or other gangue may constitute such an environment for the oxidation of sphalerite and galena where pyrite or other contaminating minerals are not present. The principal difference to be expected in the oxidation products in limestone areas, for example, where iron-bearing solutions were not present, would be a greater development of carbonates, since circulating waters much of the time probably would be saturated with CO_2. Migration of the zinc and lead could proceed the same as in a quartz gangue, and might be accelerated by saturation of the solutions by CO_2; but also might be retarded by the neutralizing effects of various impurities usually present in limestone.

Oxidation in the Presence of Admixed Pyrite.

Where limonite remains in the croppings in the place of former zinc or lead minerals, some external source has supplied the iron. Usually this source is admixed pyrite, or iron imported in solution from outside areas, ordinarily as ferric sulphate.

Admixed pyrite, as already stated, is present with sphalerite and galena in environments of moderately slow and rapid neutralizer much more commonly than in quartz gangues, and this is one reason why the limonite types characteristic of sphalerite and galena are most often found in such environments. Another important reason of course is that neutralizer exists there to precipitate iron that may be present in the solutions.

In inert gangues, sphalerite and galena, even when admixed with pyrite, do not ordinarily leave limonite. At Bisbee, for example, most oxidized lead deposits in the silica-breccias consist of cerusite with very little limonite. But a distinct fringe of exotic limonite occurs at the silica-limestone contacts farther out, showing that iron, presumably derived from pyrite, was exported and precipitated as soon as the solutions reached a neutralizing gangue.

When either pyrite or other sulphides are admixed with sphal-

erite and galena, and oxidation proceeds, various oxidation potentials are brought into play that hasten the reactions as well as influence the final products formed.

Pyrite is known to hasten the reactions. Copper salts are known to hasten them even more than pyrite, but the rate of acceleration due to the copper salts has not been determined.

Pyrite oxidizes according to the equation

$$2FeS_2 + 15O + H_2O = Fe_2(SO_4)_3 + H_2SO_4.$$

Irrespective of any reactions between the resulting ferric sulphate and the oxidation products of sphalerite and galena, the ferric sulphate itself may produce limonite either by neutralization, by dilution, or by hydrolysis. Limonite therefore may be formed and precipitated from oxidizing pyrite admixed with sphalerite and galena without the sphalerite or galena being involved, or without the limonite in any way representing oxidation of the zinc or lead minerals.

Where pyrite is admixed with sphalerite or galena it is probable, however, that inter-reaction of the respective oxidation solutions occurs.

The ferric sulphate derived from the oxidizing pyrite (or imported from outside sources) probably would react with sphalerite and galena thus:

$$Fe_2(SO_4)_3 + ZnS + 3O + H_2O = ZnSO_4 + 2FeSO_4 + H_2SO_4,$$

$$Fe_2(SO_4)_3 + PbS + 3O + H_2O = PbSO_4 + 2FeSO_4 + H_2SO_4.$$

According to these equations 1 pyrite would oxidize 1/2 sphalerite or 1/2 galena. $2FeSO_4$ and $1H_2SO_4$ would be left.

The ferrous sulphate may be oxidized by air to the ferric state in a neutral solution thus

$$FeSO_4 + 1/2O = 1/3Fe_2(SO_4)_3 + 1/6Fe_2O_3$$

and again provide a source of limonite. Or, in the absence of neutralizers or extreme dilution, the H_2SO_4 left over would

maintain an acid condition so that the ferrous sulphate would be exported from the limits of the oxidizing body, instead of having its iron precipitated as limonite within those limits. This probably was the condition referred to at Bisbee.

Again, even though pyrite is admixed with sphalerite or galena, either of the latter sulphides may oxidize to the sulphate or carbonate state by ordinary air-water oxidation processes. Excess ferric sulphate left over from the oxidation of the pyrite could react with the resulting zinc and lead carbonates, probably thus:

$$3ZnCO_3 + Fe_2(SO_4)_3 + 6H_2O = 3ZnSO_4 + 2Fe(OH)_3 + 3H_2O + 3CO_2,$$

$$3PbCO_3 + Fe_2(SO_4)_3 + 6H_2O = 3PbSO_4 + 2Fe(OH)_3 + 3H_2O + 3CO_2.$$

The ferric hydroxide, which may not necessarily exist in the solid state, would leave limonite thus:

$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O.$$

According to these hypothetical equations, limonite could be precipitated from attack upon the zinc and lead carbonates, and 1 pyrite reacting with 1 1/2 zinc or lead carbonate would produce 1/2 limonite.

Without considering the effects of possible foreign substances imported in solution, any or all of the following conditions therefore might result from the oxidation of sphalerite or galena admixed with pyrite.

1. The sphalerite or galena, independently of the pyrite, might oxidize by air-water processes alone, the zinc minerals being exported, the lead mostly remaining as sulphate or carbonate, but in both cases, no limonite would be left.

2. The pyrite might oxidize independently of the sphalerite and galena and either export its iron, leaving no limonite, or through hydrolysis of the ferric sulphate, precipitate limonite.

3. The ferric sulphate might attack the sphalerite and galena, forming their sulphate equivalents and ferrous sulphate, and the ferrous sulphate might be exported or might oxidize to ferric sulphate and limonite.

4. The ferric sulphate, from whichever of several possible sources it was derived, might attack the zinc or lead carbonates, forming their respective sulphates and ferric hydroxide, from which limonite would be precipitated.

Field evidence favors (4) as the most probable and common source for limonites derived from zinc and lead minerals.

Where strong neutralizer existed, as in limestone areas, the processes would become more complicated.

Where solutions from admixed oxidizing chalcopyrite and sulphides other than pyrite, from the complex sulphides, or from gangue minerals other than CaCO, were imported during oxidation, the processes would become even more complicated.

Disregarding these complications, and considering only the normal oxidation of sphalerite and galena admixed with pyrite, conditions could exist under which all the iron might be exported or all of it left as limonite. Even when thus simplified, so many variables are involved in the reactions, such as the rate and degree of neutralization, amount of dilution, speed of oxidation, and interaction of the various oxidation solutions, that no approximately constant ratio would be expected between the amount of limonite left in the cropping and the original pyrite-sphalerite or pyrite-galena ratios, such as has been found in the field to exist with a show of consistency in the case of certain mixtures of pyrite and the copper and copper-iron sulphides.

Field evidence certainly has failed to disclose any such approach to constancy in the case of pyrite-sphalerite and pyrite-galena mixtures; the only dependable field facts being: (1) that where pyrite is admixed with either sphalerite or galena, but does not constitute more than one fourth the total volume, one or more of the respective sphalerite or galena types of limonite usually is well developed in the place of the former sphalerite or galena nodule, and in approximately corresponding volume; so that a quantitative estimate of the former sphalerite or galena content is possible; (2) that as the pyrite content increases, the same volume of limonite may be left as in (1) above, but the distinctive limonite types characteristic of sphalerite and galena become less definite

in outline; until (3) when the pyrite content predominates over that of the sphalerite or galena, the sphalerite and galena limonite types become obscured and coated over with the smeary limonitic types of massive pyrite derivation to such an extent, that although they remain as evidence that these sulphides once were present in the cropping, no quantitative estimate of the former amount of sphalerite or galena is possible.

These conditions of course apply to deposits in environments of rapid and moderately slow neutralizer, from which the iron is not so likely to be exported as from inert environments.

Effects of Isomorphous Iron-Bearing Sphalerite.

Where sphalerite carries isomorphous iron, it seems probable that this iron may constitute one of the sources for limonite. Few cases have been observed by the writers of isomorphous sphalerite which did not also carry admixed pyrite, and there consequently does not as yet exist sufficient field evidence to justify a firm opinion regarding the part played by isomorphous iron in the production of limonite.

A Suggested Explanation for the Frequent Comparative Emptiness of the Cellular Structures.

Morse believes, partly on the basis of field and laboratory observations he has made, partly from hypothetical considerations, that, with other conditions equal, sphalerite and galena oxidize before pyrite; that the soluble iron is produced largely after the oxidation of zinc (first) and lead (second) is well finished; and that the characteristic limonites are the result of reactions of iron-bearing solutions with the carbonates of zinc and lead.

Unfortunately, the conditions of oxidation prevailing at a given place in Nature, even from grain to grain of the same sulphide mass, may vary so greatly that an absolute check on this point is difficult; but the opinion coincides with the writers' field observations insofar as limonites derived from sphalerite and galena are usually the result of attack by iron-bearing solutions upon the carbonates, rather than upon the sulphide minerals, even though

formation of limonite from direct attack by iron-bearing solutions upon the sulphides is theoretically possible, and to some extent probably takes place.

If Morse's assumption is correct, it offers a credible explanation for the frequent comparative emptiness of cells in the various cellular limonite structures, not only of the zinc and lead minerals but particularly of the chalcopyrite-pyrite mixtures. For it suggests that much of the cellular limonitic jasper webwork formed along fractures and around sulphide grains in the early stages of oxidation, and usually carrying appreciable silica, may represent limonite from imported and therefore more probably impure iron-bearing solutions. Limonite left within particular cells, on the other hand, may represent iron from solutions generated within the particular sulphide grain or area and this would account for its lower content of silica and other impurities commonly found in the webwork or cellular mass. If the solutions generated within the intercellular spaces were derived largely from pyrite after most of the other sulphides had been oxidized, their acidity would be high, and much of the iron in those solutions, in the absence of strong neutralizer, would stand a good chance of being exported instead of being precipitated within the cell as limonite. In the case of zinc minerals, the greater solubility of these over the lead minerals, would of course explain in part the greater emptiness of cells in structures derived from them.

Reasoning in a matter like this becomes involved, and the explanation suggested at best offers only one of several for the frequent comparative emptiness of cells in cellular structures derived from sulphide masses low in pyrite. The idea is, however, sufficiently credible to merit thorough field and laboratory investigation.

SUMMARY.

1. Unlike the copper and copper-iron sulphides, sphalerite and galena may dissolve without generation of or attack by iron-bearing solutions, and commonly do so. In such case they leave no limonite.

2. If limonite is left, it signifies that the sulphides carried ad-

mixed pyrite, or other iron-yielding minerals, or that iron-bearing solutions were imported during oxidation of the zinc or lead minerals.

3. In inert environments usually little limonite is left even if admixed pyrite was present.

4. In environments of rapid or moderately slow neutralizer, sphalerite and galena more commonly carry admixtures of iron-yielding minerals, and in such environments both sulphides usually leave distinctive limonite products. The physical characteristics of these serve to distinguish them from each other and from certain other limonite types which they somewhat resemble.

5. In environments of rapid neutralizers, the distinctive limonite types left by both sphalerite and galena usually are masked to some extent by a fluffy, pulverulent limonite which adds to the difficulty of reading the leached cropping.

6. No approach to constancy of ratios has been found in the field between the amount of limonite left in any given case and the original sphalerite-pyrite or galena-pyrite ratios. But where the pyrite did not exceed, roughly, one fourth the original sulphide volume, the characteristic porous zinc or lead limonite products usually fill the place of the former sulphide, so that an approximate estimate of the former zinc or lead content is possible. As the pyrite content increases, and particularly when it exceeds that of the respective zinc or lead sulphides, the same volume of limonite may remain, but the types indicative of zinc or lead usually are so crusted over or otherwise obscured by limonites of pyrite origin that no quantitative estimate of the former zinc or lead content of the cropping is possible. Usually all that can be safely inferred is that zinc or lead minerals in some indefinite amount were formerly present.

7. In sphalerite-galena mixtures, or in mixtures made up of sphalerite-galena-chalcopyrite combinations, where these sulphides occur as nodules greater than 1/2 centimeter long, limonites characteristic of the respective sulphides usually are left indigenous to the areas from which they were derived. The oxidation products of the different sulphides in such case do not ordi-

narily "mix" enough to cause much confusion in interpreting the cropping, and a roughly approximate estimate of the former content of any or all these sulphides often is possible. But, as stated in (6) above, as admixed pyrite approaches or exceeds one fourth the total sulphide volume, the limonites indicative of sphalerite, galena, or chalcopyrite in such mixtures become more difficult to read, and the difficulty increases in direct ratio to increase in pyrite content of the original sulphide body.

8. For reasons that are discussed, neither primary nor secondary zinc minerals are as likely to remain in a leached cropping as are primary and secondary lead minerals, once oxidation is well advanced.

DUNCAN, ARIZONA.

BIOGENESIS OF HYDROCARBONS BY DIATOMS.

C. F. TOLMAN.

INTRODUCTION.

THIS paper summarizes certain tentative conclusions which are derived from microscopic and field studies of the sedimentary rocks of California oil fields carried on since 1914, and from preliminary data derived from the study of epidemics of freshwater and marine diatoms by Becking and McMillin in 1925, by Becking, McMillin, Field and Tolman in 1926, and from chemical studies by Todachi Hashimoto in 1926–27 of diatom oil derived from material collected at Copalis Beach.*

As Dr. L. B. Becking and the writer have received financial support in carrying on the study of diatoms, from the Research Fund (this investigation is known as Project No. 5), administered by the American Petroleum Institute, this paper is written to summarize the status of the investigation reached at the time when funds became available for more detailed and systematic work.

Responsibility for the emphasis on the biogenetic processes must rest on the author of this paper, and not on his associates, who are carrying on their biological and chemical studies without any preconceived notions of the bearing of the research on the problem of the origin of oil, and have first directed their attention to the oil formed by the diatoms because the process has been observed by us, and can be studied under extremely favorable conditions at Copalis Beach, Washington. In the work now in progress large amounts of pure diatom culture will be collected in order to obtain the large amount of oil necessary for accurate and detailed chemical study. Later on attention will be directed to the chlorophyll of the diatom, the products of bacterial decom-

* See companion paper, "Preliminary Statement Regarding the Diatom Epidemics at Copalis Beach, Washington," by Becking, Tolman, McMillin, Field and Hashimoto. ECON. GEOL., vol. 22, pp. 356–368, 1927.

position of the chlorophyll, and the study of the fatty acids, the sulphur compounds, and other constituents of the diatom extract.

The writer of the present paper believes, however, that the preliminary biological and chemical studies of his associates, combined with the results of field and microscopic study of the fossil diatomaceous sediments of California furnish data strongly indicative of the importance of the process of direct manufacture of hydrocarbon oils by diatoms. This is a biogenetic process. The oil is manufactured by the chlorophyll bodies enclosed in the diatom test. The energy necessary for the chlorophyll to break up carbon dioxide (or bicarbonates), and water, and form organic compounds of higher energy content (in this case hydrocarbons), comes from the sunlight, which " activates " the chlorophyll.

Direct vital manufacture of oil has actually been observed by us, and this observable method of genesis may be denominated " biogenesis," in contradistinction to the genetic processes of bacterial decay and of destructive distillation, one or both of which have been adopted in the formulation of the majority of theories on the origin of oil, and neither of which has as yet been actually observed employed by nature in the manufacture of oil, and therefore may be considered theoretical.

The purpose of this paper is to summarize the relation of the fossilized Tertiary diatomaceous sediments to the oil contained therein and in the overlying clastic sediments. Before this can be accomplished satisfactorily, it is necessary to review our knowledge of these organic sediments, especially in regard to their extent and their character, to find out whether they are of deep water or shallow origin; whether they are marine or estuarine; also to understand the processes of sedimentation which control their accumulation, and the retention of the hydrocarbons; and finally to know what the microscope shows regarding the constituents of the organic opal shales (" bituminous shales "), their consolidation, diagenesis and metamorphism.

SUMMARY OF DATA PRESENTED AT THE SYMPOSIUM ON THE ORGANIC SILICEOUS SHALES, GEOLOGICAL SOCIETY OF AMERICA, CORDILLERAN SECTION, JAN. 29, 1926.

Appreciating the necessity of disabusing the minds of geologists familiar with California geology of certain rather widely accepted but erroneous notions regarding the "diatomaceous formations" of California, and of summarizing the facts that may now be accepted as established, the writer called a symposium "on the siliceous shales and the origin of oil in California" which was held at a meeting of the Cordilleran section of the Geological Society of America, January 29, 1926. A brief outline of the papers presented at the symposium, and of the discussion which followed their presentation was compiled by the present writer in collaboration with the authors of each paper.

As this outline has not as yet been published, the writer here attempts to bring out the salient features of this conference by giving brief excerpts from the authors' summaries.

In opening the symposium, C. F. Tolman emphasized the great extent and thickness of the Tertiary opal or diatomaceous sediments and stated that they had not received the attention from geologists that their importance demanded.

We have a great series of opal and chalcedony-bearing sediments which vary greatly in appearance and physical constitution, the varieties of which have not received appropriate names. They include a series of diagenetic and metamorphic rocks, which as yet have received incomplete study and description. The sedimentation problems have scarcely been mentioned in the literature. Numerous papers regarding the relation of these rocks to the origin of oil have appeared, but the presentation of such papers is premature since it was not preceeded by a thorough study of the processes of sedimentation, diagenesis, and metamorphism of the organic siliceous sediments.

Dr. Austin F. Rogers discussed "Opal and its Relation to Other Forms of Silica." This paper was the first of the series because the so-called diatomaceous shales are composed largely of either opal or chalcedony, or mixtures of the two. Rogers stated, in part:

Opal is one of the seven or eight forms of silica found in nature. It is probably a hardened hydrogel in which there were originally two phases, silica and water. By the gradual diffusion of the water into the silica a solid solution was formed. The formula of opal may be expressed thus: $SiO_2(H_2O)_x$ where x is variable.

Opal is amorphous, though like many other amorphous minerals it often shows double refraction due to strain set up in the hardening of the gel. Unlike other forms of silica it gives no X-ray diffraction pattern.

Diatoms, radiolarians, and certain types of sponges secrete silica in the form of opal.

In order that some idea of the stratigraphy and great thickness of these opal sediments might be recalled to the members of the symposium, Dr. R. N. Nelson discussed "Distribution and Thickness of Diatomaceous Shales."

The Moreno shale (upper Cretaceous) at Coalinga is known to be diatomaceous. However, the most important diatomaceous shale deposits of California occur in the Tertiary. The earliest of these is the Kreyenhagen shale, considered by some to be Oligocene, and by others Eocene in age. Exposures of this shale are found on the western side of the San Joaquin Valley from San Emigdio, at the extreme south, to the north side of Mt. Diablo, at the north. The shale has a thickness of from 400 to over 1,000 feet at Coalinga. On the north side of Mt. Diablo it is 500 feet thick.

The next younger diatomaceous shale is the Monterey shale (middle Miocene) which occurs on the west side of the Coast Ranges. The northermost exposure is at Point Arena where it has a thickness, including some sandstone, of 5,000 feet. Southward, at Point Reyes, the shale is 4,000 feet thick. There is also some evidence of the existence of the Monterey shale near Petaluma. In the Berkeley Hills, the Monterey series includes three siliceous shale members separated by sandstones. The Monterey shale occurs in considerable amount in the Santa Cruz Mountains. Still farther south, its correlative, the Salinas shale, over 4,000 feet thick, is extensively exposed in the Salinas Valley. In the Santa Maria district, the Monterey shale is widespread and up to 4,200 feet thick. This does not include the upper Miocene and Pliocene organic sediments. In the Cuyama Valley, the Salinas shale, also called the Maricopa shale, is 2,000 feet thick. Along the Santa Ynez River to the south, the shale has a thickness of up to 2,000 feet. Monterey shale is also found along the Coast near Santa Barbara. The lower part of the Maricopa shale on the southwest side of the San Joaquin Valley is considered to be middle Miocene in age and approximately 2,800 feet thick.

A small amount of diatomaceous shale is included in the Tembler (middle Miocene) at Kern River on the east side of the San Joaquin Valley. In the Los Angeles district, the Puente shale is believed partly equivalent to the Monterey shale. The Puente shale has been divided into two parts, the lower of which is at least 2,000 feet thick, and the upper at least 400 feet thick.

In the upper Miocene, the northermost occurrence is the Hercules shale member of the Briones formation in the Concord quadrangle. It is about 500 feet thick. Southward, diatomaceous shales are found in the Santa Margarita, upper Miocene, as follows: Salinas Valley, over 400 feet thick; Cuyama Valley, a few hundred to 1,500 feet thick. Along the upper Santa Ynez River diatomaceous shale occurs at the top of the Tequepis sandstone, a possible equivalent to the Santa Margarita. In the Santa Clara Valley of southern California, the Modelo formation, upper Miocene, covers wide areas. On the north side of the valley, it includes diatomaceous shales aggregating from 2,000 to 4,300 feet in thickness; on the south side, from 2,000 to 3,200 feet. The upper part of the Puente shale of Los Angeles is probably equivalent to a part of the Modelo formation.

Pliocene deposits of diatomaceous shale have been described from the Purissima formation at Half Moon Bay, from the Fernando of the Purissima Hills in the Santa Maria District, and from the Pico formation of Fernando Valley.

With possibly few exceptions, all of the above deposits of diatomaceous shale are associated with petroleum or bituminous matter.

In addition to the localities mentioned by Mr. Nelson, Frank M. Anderson mentioned the occurrence of Miocene diatomaceous shales in Humboldt County.

On account of the importance of the opal sediments in the Santa Maria district, the great thickness of the organic formations present there, and the positive relation of the diatomaceous formations to oil, Mr. B. F. Hake presented a paper entitled "Occurrences of Siliceous Shales in the Santa Maria Basin," and presented the following geological column for the Santa Maria district. This stratigraphic column was the result of detailed geological work by C. F. Tolman and B. F. Hake on the Santa Maria district, and this publication is due to the courtesy of the Marland Oil Company.

Recent	Alluvium	Sandy loam.
Quaternary	Terraces	Sand, pebbly brown.
Pliocene 1400 ft.	Fernando (Upper)	Sandstone, clay, conglomerate, freshwater limestone.
	Fernando (Lower)	Massive yellow sandstone.
Pliocene	Foxen 750 ft.	Fine sandstone and diatomite.
Miocene or Pliocene	Harris 2000 ft.	Massive diatomite. No oil except along fracture zones.
Lower Miocene	Monterey 4200 ft.	(*a*1) Diatomaceous shale, glassy opal, slightly petroliferous.
		(*a*2) Diatomaceous shale, argillaceous, slightly petroliferous.
		(*a*3) Slabby diatomaceous shale, highly petroliferous.
		(*b*) Hard diatomaceous shale, opal, chalcedony, highly petroliferous.
		(*c*) Flints and opal with diatomaceous shale, highly petroliferous.
		(*d*) Diatomaceous shale with siliceous dolomite.
.....		
Miocene?	Lospe 2,700 ft.	(*a*) Black shale, gray sandstone, with gypsum and calcite.
		(*b*) Diabase.
		(*c*) Black shale, slabby green sandstone.
		(*d*) Gray, gypsiferous shale, slabby sandstone.
		(*e*) Rhyolite tuffs.
		(*f*) Gray shale, hard sandstone.
		(*g*) Grayish-green sandstone and shale.
		(*h*) Red and green sandstone and conglomerate.

In order to obtain some idea as to the physical conditions under which the California organic shales have been deposited, Dr. David Starr Jordan discussed, " Fossil Fish and Their Bearing on Siliceous Shales."

He brought out that of the hundred species of fish found in the diatomaceous shales, about six or eight species might be

classified as of deep-sea type, and that most of the species were shore fishes. On the whole, the evidence suggested shallow-water deposition along the coastline, or in bays and estuaries. Dr. Loye Miller discussed fossil birds and their bearing on siliceous shales. He mentioned 17 species of birds which represented more or less completely articulated skeletons or parts of skeletons. The birds had been entombed in sprawling attitudes within a matrix of diatomaceous ooze. Dr. Davis inquired of Dr. Miller as to how far off-shore the birds lived. Dr. Miller replied that the gannets lived near the shore and the headlands; that the shearwaters lived some distance off shore, but frequently came in, usually as floating dead bodies.

Dr. H. G. Schenck discussed diatomaceous shales interbedded with arkose, in order to bring out the conditions of sedimentation which are frequently observed on the margins of basins carrying diatomaceous sediments. He described details of the stratigraphy of an occurrence of arkose interstratified with diatomite, in Bear Valley, San Benito County, California, and described six layers of arkosic sandstone interlaminated with pure diatomaceous shale. The shallow water origin of this deposit cannot be doubted. Other deposits of interstratified arkose and diatomite, and conglomerate and diatomite were mentioned in the symposium.

Mr. Frank M. Anderson described a repetition of thick beds of conglomerate with beds of diatomaceous shale between them, in Kern County. Dr. Robert Anderson mentioned an occurrence of huge boulders of granite in the diatomaceous shale along the border of the Carrizo Plains, on the west side of the Temblor range. Also, in the region north of Coalinga, Anderson and Pack found thin beds of sand of a somewhat arkosic type interbedded with the Kreyenhagen shales. Dr. Schenck mentioned fossilized mud cracks found in diatomaceous shales in the Cuyama district.

The general purport of this discussion was to emphasize the fact that Tertiary organic opal formations of California were laid down in relatively shallow basins, and the diatomaceous sedi-

ments often extended up to the shore line of the basins. These data were important in disabusing the minds of those present of the notion formerly quite prevalent, that marine diatomaceous deposits were deposited exclusively in deep water.

Papers relating to the origin of oil were given by F. M. Anderson and Robert Anderson, and G. C. Gester. Frank Anderson gave a paper entitled "History of Theories Regarding Siliceous Shales and the Origin of Oil." This paper has been elaborated and published under the title "Origin of California Petroleum."[1] It contains an excellent summary and bibliography of the subject and especially of the "diatom theory," credit for which is given to J. D. Whitney (1865). References cited by Anderson will not be repeated in this preliminary paper. Robert Anderson gave a paper entitled, "The Origin of Oil from Marine Plankton Shales in California." This paper was especially valuable, because it summarized the final conclusions of the pioneers in California petroleum geology, Ralph Arnold and Robert Anderson. The author's abstract of this paper is as follows:

> The theory is here reaffirmed that most of the oil in California originates in the shales characterized by the remains of minute marine organisms, chiefly diatoms and foraminifers. This theory, originally founded on the close relation of petroleum deposits and seepages to what was regarded as one formation of such shale, of Miocene age, was by successive steps confirmed through the discovery of several thick formations of similar character but different age, ranging from upper Cretaceous to upper Miocene, with each of which petroleum is intimately associated. These formations comprise thicknesses of organic shale ranging from a thousand to over five thousand feet.
>
> In the Santa Maria oil field the principal oil bearing formation is the Monterey shale (middle Miocene). In the Coalinga fields the principal shales are not Monterey, but Kreyenhagen, of Oligocene age. A lower formation of diatomaceous shale, the Moreno, also oil bearing, is of Cretaceous age. Each of these two horizons in the Coalinga field has its own type of oil. In the Temblor Range and the Southern California fields there are important oil-yielding shales of similar constitution dating from the upper Miocene.
>
> Thus there are at least four distinct formations of this type of plankton shale, representing different periods of deposition, but each showing a

[1] *Bull. Geol. Soc. Am.*, 37, pp. 585–614, 1926.

petroliferous character and standing in the position of mother rock for large accumulations of oil.

Aside from these accumulations in the oil fields, the wide-spread occurrence of oil in the shales gives strong evidence of its indigenous origin. In the aggregate there are many thousands of miles of such shale outcrops, which characteristically show evidences of oil. At least as far north as Point Arena such shales occur and are bituminous, and at the next occurrence to the south, at Point Reyes, they are again oily. Some of the principal indications are . . . discoloration due to oil, evidence of the bituminous nature of the shales on being heated, seepages, veins and cavities filled with oil, interbedded sandstones impregnated with oil or asphalt.

The volume of organic debris represented by these deposits is enormous. They are largely composed of diatom tests and the derived silica, but foraminifera are an important constituent and are to be considered along with the diatoms as having been a source of oil.

The petroliferous character of the shales prevails regardless of a great variety of relationships to other strata. For instance, in places in the Santa Cruz and Salinas Valley regions the oil bearing shales lie, as they were deposited, on granite. Elsewhere where lying between other formations, the shales have their characteristic petroliferous nature, whereas the other strata rarely contain indications of oil except within a comparatively short distance from the shales.

Thus, combining the various different lines of evidence, no doubt can remain that the great bulk of the petroleum of California originated in this type of shale.

Finally a valuable summary of relations of oil fields to structure and formation was given by G. C. Gester, who emphasized that

Too much has been taken for granted and not enough real work done, nor thought given to the problems connected with the origin and accumulation of oil in California. This paper presents a plea that more consideration should be given to these problems, both for the benefit of pure science, as well as for the more practical purpose of aiding in the discovery of new oil fields.

He summarized the age of the source rock:

Age of Source Rocks

Miocene	Oligocene	Eocene	Cretaceous
74.5%	4.2%	19.2%	2.1%

There are also six fields where the Pliocene contains strata which might be classed as source rock.

In practically all of the California fields there are thick shale formations more or less intimately associated with oil bearing horizons. In a number of cases, however, there are hundreds of feet of clays and clay shales, with occasional sandy beds between the top of the shales and the base of the oil measures. In other cases the oil measures themselves rest on the shale formations.

In practically all fields it is noted that the thick shales underlie the reservoirs which are near shore sand and sandy shale deposits. The general unconformity at the top of the shales in each case is regional, and sandstones lie on bevelled shales. The unconformity is also shown by change in form. If the shales are the source of the oil, the question is raised as to how and when the change took place from the original organic material, and what were the factors governing its migration from the source into the reservoir rock.

The Miocene shales have been classed in California as being the most important source rock. These shales attain thicknesses of over 5,000 feet. In some localities they contain a little oil in a free state; in other places, oil can be derived from the shales only by distillation processes. In many localities, however, no oil can be obtained from the shales by either titration or distillation. In some cases the latter condition is true of the shales which immediately underlie oil measures. Furthermore, some of these shales are highly diatomaceous. In other places they are almost devoid of fossil remains. It is further interesting to note that there are cases where rich diatomaceous shales hundreds of feet thick are overlain by an adequate reservoir rock in which there are favorable structural conditions that have been adequately tested and no oil found.

In other localities comparatively small thicknesses of foraminiferous shales are found immediately associated with the oil measures. These are in turn separated from formations of diatomaceous shales by several hundred feet of sediments.

The data presented are somewhat conflicting, and the question arises—were the diatoms in part or the only ultimate source of the oil, or should we look further for some other type of organic matter from which the bulk of the California oil may have had its origin?

The question propounded by Mr. Gester in the last sentence quoted is taken as the subject of the following section of this paper.

ARE DIATOMS THE CHIEF SOURCE OF CALIFORNIA OIL?

The results of the symposium brought out clearly that the geologists who have studied the organic opal shales of California, and their relations to oil are unanimous in the conclusion that oil has been derived from these organic shale formations. Perusal of the literature, and personal conversation with most of the men who have worked in the field has brought out, however, a difference in opinion as to the importance of the diatom itself in the segregation and formation of the oil.

In 1893 A. C. Lawson[2] described the "bituminous shale" (that is, Monterey, shale), as the source of the asphaltum deposits associated with this formation. He states that the white shale is very porous, the pores being molds of small bivalves—foraminifera and occasionally a mollusc. These calcareous shells have been dissolved out. There are occasional deposits of "infusorial earth" but not extensive. He believes siliceous rocks to be of volcanic rather than of organic origin; and carbonaceous remains to be due to small animals. Lawson himself is not positive, but suggests the advisability of questioning the diatom theory, or indeed organic origin of siliceous shales of that character.

Since this publication, a number of geologists, possibly influenced by Dr. Lawson's conclusions, have been rather skeptical as to the importance of the diatom in the secretion of oil.[2a] Even the proponents of the theory, Ralph Arnold and Arnold and Anderson,[3] have been very conservative in their statements as to

[2] Lawson, A. C., Univ. Calif., *Bull. Dept. Geol. Sci.*, vol. I., No. 1, pp. 1–59.

[2a] Pack, R. W., "The Sunset-Midway Oil Field, California," U. S. Geol. Surv. Prof. Paper 116, p. 10, 1920. Stalder, Walter "A Section of the Monterey (Salinas) Shales in Pine Canyon, Monterey County, California," *Bull. Am. Assoc. Pet. Geol.*, 8, p. 55, 1924. Cunningham, George M., "Were Diatoms the Chief Source of California Oil?" *Bull. Am. Assoc. Pet. Geol.*, 10, pp. 709–721, 1926.

[3] Arnold, R., and Anderson, R., U. S. G. S. Bull. 317; Arnold, R., and Anderson, R., U. S. G. S. Bull. 322; Arnold, R., Two Decades of Petroleum Geology, 1903–22, *Bull. Amer. Assoc. Petrol Geol.*, VII., 6, pp. 603–624, 1923. Arnold, R., U. S. G. S. Bull. 321, p. 121, 1907. Eldridge, G. H. and Arnold, R., U. S. G. S. Bull. 309, 1907. Arnold, R., and Garfias, W. R., *Amer. Inst. Min. Eng.*, Bull 87, pp. 383–470, 1914. Arnold, R., and Johnson, R., U. S. G. S. Bull. 406, 1910.

the rôle played by the diatom itself, and all writers without exception have suggested decomposition of organic material enclosed in the organic shales as an important source of the oil.

It has long been known that diatoms secrete oil. Juday, in his work on freshwater plankton,[4] states that: "The diatom sample contained a larger percentage of ether extract than any other plant material." Brandt finds [5] 9 per cent. ether extract in marine diatoms.

A Mann [6] states:

> Living diatom plants will always be found to contain from two to ten shining oil globules. The bulk of this oil, in proportion to the size of the diatom, rarely falls below 5 per cent.; and the author has samples of diatom material in which a careful measurement of the contained oil shows a proportion of 50 per cent.

In spite of these and many other observations of like kind, there has been a curious unwillingness to consider the diatom as the sole or chief source of the oil found in diatomaceous formations, and in the adjacent clastic rocks. The reasons for this attitude appear to be as follows:

1. Throughout much of the organic opal shales recognizable diatoms are scarce. The dense splintery or porcellaneous opal shales are usually rich in bitumin but poor in well-preserved diatom tests.

2. In the upper portion of the Tertiary organic formations of California, diatomite and diatomaceous earth are abundant, often consisting wholly of perfect and fragmentary diatom shells. These formations are, as a rule, barren in hydrocarbons, and it would seem that where diatoms are abundant there is no oil; where diatom shells cannot be recognized, oil residues are abundant. This is probably the main reason for the questioning of diatoms as the source of oil, and discussion of this relation will be taken up again after a description of the microscopic characteristics of diatomaceous formations has been considered.

[4] Chancey Juday, Wisconsin Survey, Bull., 1922.

[5] Brandt. *Wiss. Meers untersuchungen Kiel.*, n. f. III., 45, 1898.

[6] Mann, A., "The Economic Importance of the Diatom," Ann. Rept. Smith. Inst., 1916, pp. 386–397.

SUMMARY OF FIELD AND MICROSCOPIC STUDY OF THE TERTIARY ORGANIC SILICEOUS SEDIMENTS OF CALIFORNIA.

The field studies of the organic opal sediments of California have been carried on in connection with the field work of the Stanford Geological Survey since 1912, and the microscopic work has proceeded in a desultory way ever since that time. Intensive study including field work followed by microscopic investigations was carried on in the San Joaquin Valley the fall of 1919, in the Santa Maria District during the fall of 1924, and in the Temblor range the summer of 1927. The study most fruitful in results was that of the Santa Maria District, the classic locality for this type of sediments, where the writer was ably assisted in the field by Mr. B. F. Hake.

The work in 1919 in the San Joaquin Valley brought out clearly that the diatomaceous earths, that is, the deposits rich in diatom tests, are peculiarly deficient in hydrocarbon residues, and appear to be barren as far as oil generating characteristics are concerned. The following quotation from a report[7] on the San Joaquin Valley work emphasizes this fact.

> The purest variety of diatomaceous shale is pure white throughout; porous, light in weight, and contains little or no oily material. It is the writer's belief that in the case of this pure dead-white material, the oil secreted by the diatoms was lost during the process of sedimentation. Hence such dry diatomaceous shale does not furnish much oil when subjected to the processes of natural distillation at depth.

These findings are in accord with the conclusions recently announced by J. R. Takahashi,[8] who finds that the pure diatomaceous earth abundant in the upper part of the Tertiary organic formations of California is barren in oil residue and probably never contained much oil.

In contrast with the barren diatom-rich earths, the dense, clay-like or porcellaneous opal shales were recognized as oil generating and the following field characteristics were given:

[7] Private Report.

[8] Takahashi, J. R., Econ. Geol., vol. 22, "Origin of California Petroleum," pp. 133–158, 1927.

The characteristic field tests and appearance indicative of the oil-generating character of shales as they appear at the surface may be summarized as follows:

The shales are:

1. Light in weight (calcareous and argillaceous shales are heavier than the diatomaceous varieties and generally are not oil-generating.
2. Non-calcareous (they do not effervesce when tested with acid).
3. Siliceous (mineral is opal and chalcedony).
4. Often waxy in appearance, and when diatomaceous, are absorptive (they stick to the tongue).
5. The weathered surface is bleached to a light color (white, yellow, light-gray, lavender and pink).
6. The fresh surface is dark brown to black.
7. The shales often have a yellow film deposited in cracks, which may be either sulphur or a mineral resembling sulphur (this mineral is jarosite, a hydrous potassium-iron sulphate).
8. Where the strata are disturbed and oil products are afforded ready escape, the adjacent formations may be cemented with brea or stained with oil.

Microscopic study of material from the Santa Maria District (1924) resulted in the following classification of the organic opal formations:[9]

1. *Diatomite (and Diatomaceous Shale).*—The term diatomite is the trade name for the pulverulent, pure diatomaceous deposits which in California occur in thick beds of great purity. Diatomaceous earth is not a satisfactory term for the California material, as the beds are massive, from ten to several hundred feet thick without lamination (see Fig. 1). For this reason the term diatomaceous shale is singularly inappropriate. The commercial term diatomite is here adopted for the massive, pulverulent, porous opal sediments composed largely of diatom "pill boxes," or broken fragments of the same set in a matrix of uncemented diatom debris (see Fig 2). The Santa Maria diatomites usually contain 1 to 5 per cent. sponge spicules, and small amounts of clear volcanic glass fragments and clayey limonitic material. High power microscopic work has shown that the matrix of

[9] Mr. Roy Collom, Chief Geologist, Marland Oil Company of California, generously granted permission to publish the scientific results of this work.

diatom debris consists largely of nob-like adornments of the *Coscinodiscus*, which form makes up at least 90 per cent. of the recognizable diatom materials, and is similar in shape and size to the *Aulacodiscus* described in the companion paper on Copalis

FIG. 1. Looking northeast from Miguelito Creek at massive diatomite, mined by Celite Products Company, near Lompoc, California. Bedded "flints," shown on left, consist largely of chalcedony. In the syncline to the right, the massive diatomite beds are 1,400 feet thick, single beds reaching a thickness of over 100 feet.

beach diatom epidemics. The diatomite is usually free from hydrocarbon oil residues and stains, except where oil has migrated into it from underlying deposits of hydrocarbons. (See Fig. 3.) In the Santa Maria District, the diatomite rarely shows lamination or shaley parting, but elsewhere, especially in the Midway-Sunset fields, the pure uncemented diatomaceous shale, composed largely of recognizable fragments of diatoms, is strongly laminated. The term diatomaceous shale should be restricted to material of the latter type.

2. Uncemented Opal Silt and Opal Shale.—The diatom debris which occurs in varying amount in the diatomites makes up the bulk of this second type of opal rock, and where this type of sediment has not been indurated or cemented, the formation has a characteristic punky or clay-like appearance. The beds may either be massive or laminated. The massive material was designated in the field as clayey or punky diatomite. Microscopic examination showed that this type contains little clay, very minor amounts of clayey limonite, occasional organic residues, and is composed al-

most entirely of the diatom debris mentioned above. Familiarity with the shape of the *Coscinodiscus* nobs made it possible to recognize most of the fragments of this debris as of this origin. These extensive siliceous formations, then, with their few recognizable fragments of diatoms and almost no perfect tests, are very largely of diatomaceous origin.

3. Cemented Opal Shales (Figs. 4, 5).—This type of organic deposit differs from the uncemented variety in that the diatom debris is cemented with opal. These rocks usually have a well-developed shaly structure, and in the field are denominated porcellaneous shales, slabby opal shales, and brittle opal shales. The bulk of the material is the diatom debris, and while the diatom nobs are more difficult to recognize, they undoubtedly make up the bulk of the material. The opal cement surrounding the grains has a slightly different index of refraction from the debris, and thus the two types of opal can often be distinguished.

The origin of the opal cement is interesting. Undoubtedly it is in part secondary, produced from the solution and recrystallization from the opal of the organic sediments. In part it may be originally deposited as an opal gel from the solution of diatom material in the ocean and reprecipitation of the opal. The form of the diatom nobs and disappearance of the thinner portion of the diatom shell suggests that solution has been active in the basins of deposition while accumulation was taking place. Moreover, vitreous opal layers that are abundant in both uncemented and cemented varieties of opal shales are believed to be in part of direct sedimentary origin, as discussed below.

In the Santa Maria region the lower portion of the organic sediments is composed largely of cemented opal shales, and the associated chalcedonic and dolomitic shales described below. These contain abundant hydrocarbon residues, and were without doubt the source rock of the petroleum deposits of the region.

4. Vitreous Opal.—In certain localities, diatomite, opal silts and cemented opal shales contain layers of vitreous opal. In the hand specimen this material is strikingly different in appearance from the rocks made up of diatom debris. Instead of a

porcellaneous or clayey appearance, they have a vitreous appearance, and they are denominated " flints " by the local inhabitants.

The vitreous opal occurs as secretions, lenticular layers, and as beds and laminae. In some cases vitreous opal layers of an inch in thickness have been traced many hundreds of feet along the strike of the beds, and laminae small fractions of an inch in width for scores of feet. While the microscopic data are inconclusive as to whether these delicate and extensive laminae are the result of an original deposition of a silica gel or an alteration of the diatom debris, the field relations point strongly to the former conclusion.

In summary, the vitreous opal is in part a replacement of diatom debris, and in part a sedimentary deposit of opal gel.

5. *Chalcedonic and Dolomitic Shales* (see Figs. 6, 7, 8, 9).— Induration and diagenesis result in the development of a series of chalcedonic and dolomitic shales, and massive beds of dense chalcedonic material. This process of induration is due to compacting, cementation by opal, and recrystallization.

The fine diatom flour packs harder with the increase in the original opal cement. Partial solution and recrystallization produces a dense porcellaneous shale, and recrystallization of the opal to chalcedony produces the contorted flints usually accompanied by dolomitic layers (see Figs. 10–13). This process consists of the recrystallization first of the opal cement into chalcedony, and later of diatom flour and diatom tests to chalcedony.

Dolomitization is common in the lower portion of the organic sediments of the Santa Maria region, and apparently is an earlier process than chalcedonization. Both types of recrystallization concentrate the impurities, and with these impurities the hydrocarbons. These impurities are driven out of the body of the chalcedony and concentrated along the boundaries of the chalcedony and the original opal which has not yet been recrystallized.

SUMMARY OF THE BEARING OF THE MICROSCOPIC DATA ON THE ORIGIN OF OIL.

The microscopic study outlined in great brevity above suggests the following in regard to the origin of oil.

The opal constituting the extensive Tertiary sediments of this type in California has been secreted largely by diatoms. Proof of this is the finding of the recognizable diatom nobs throughout all types of Tertiary opal shales except those that have been thoroughly recrystallized.

Both Lawson [10] and L. C. Takahashi [10] were inclined to ascribe the origin of petroleum to unknown organisms. The only abundant organic sources of silica that can be thought of are silico-flagellates, sponges, and radiolaria. None of these occur in sufficient abundance to account reasonably for the vast amount of silica in the organic formations. With the present knowledge of the "bituminous shales" of California, a volcanic or hot spring origin of the opal does not appear to the writer to be tenable. Since this great amount of silica is secreted by the diatoms, they would be the organisms to which one would reasonably attribute the hydrocarbons.

We know of no "unknown organisms" rich in oil that are likely to be an important constituent of diatom-rich plankton. The analysis of various authors as compiled by Juday [11] shows that there is a significant difference in the oil content of green, blue-green and brown algae (5–9 per cent.), and that of diatoms (over 22 per cent. of dry organic matter). An analysis by Brandt, (cited by Judây), of certain *Peridiniales* which form an important constituent of marine plankton, seems to indicate that these organisms form very little oil in the cell ($\pm$ 5 per cent.).

Crustaceans and fishes may have high fat content (but not a high hydrocarbon content), but it is not reasonable to believe that a sufficient number of these organisms ever existed in the extensive opal shales of California to develop the great amount of oil and at the same time for their remains to have largely disappeared. Foramanifera are fairly abundant, and may contribute oil in a minor way, and locally be important, but do they form oil? [12]

It appears that those strata composed of perfect diatom shells are poor in hydrocarbons, while those composed of finer com-

[10] *Loc. cit.*

[11] Chancey Juday. Wisconsin Survey, Bull. 64, 1922.

[12] Anderson, F. M., *op. cit.*, p. 599.

minuted diatom debris are oil generators. This suggests that there must be some process of sedimentation which results in the complete loss of the hydrocarbons under conditions which preserve the shell, and preservation of the hydrocarbons under conditions which destroy the shell.

It would appear that the diatomites are accumulations largely of empty shells of the dead organisms, while accumulations of diatom debris with colloidal matter have preserved the oil. Our studies at Copalis Beach furnished significant data along this line. It appears that there is a varying amount of diatom oil in the organism during various stages of the epidemic; that the amount increases after a period of sunlight. If the tests are broken up and the oil driven into the colloidal material at the time they are full of oil, an abundant supply of hydrocarbons would be absorbed in the colloidal material that is later consolidated. On the other hand, under quiet conditions, the organism may live and consume the store of hydrocarbons in the vital processes, especially in spore formation, and finally dying, the empty shells accumulate on the ocean bottom, forming barren diatomite. The observation that the living diatom explodes when immersed in fresh water is of great importance. (See companion paper.) The osmotic pressure of the cell sap is sufficient, when the diatom is immersed in fresh water, to break the brittle shell and drive out the oil into the adjacent colloidal material, of whatever type it may be. A sufficient change in salinity in estuaries and bays at times of floods might produce this phenomenon. Possibly other process also can break up the shell and drive out the oil at the time the diatom is well supplied with that material. The excessive formation of hydrocarbons might itself break open the siliceous container. In any case, we have actually seen the process under action whereby the hydrocarbons formed directly by the diatoms can be driven out of their shells into the surrounding medium (see Figs. 8–11, previous companion paper).

Finally, the analysis of the diatom oil shows a large amount of pure hydrocarbon oil and also an interesting sulphur compound. The latter may explain the sulphur rich character of certain

California oils. Doubtless a complete analysis of a larger amount of the diatom oil will throw further light on the composition of California oils.

The dark waxy carbonaceous residue found in most of the oil generating formations from which hydrocarbons have been distilled (the brown and black shales of the California oil well drillers), may represent the decomposition of chlorophyll and other organic compounds.

The character of the deposit of a diatom rich plankton would of course be colloidal, and these colloids would have high absorptive powers for the oils. There must be some special conditions controlling sedimentation to drive out the oil from the diatom test at the proper time and absorb it in the colloidal mass. Moreover, all diatomaceous formations are not rich in oil, and all have not developed commercial pools of oil. In such basins the conditions of sedimentation were unfavorable for oil preservation.

The determination of just what the favorable conditions may be will be of great interest. A series of oil-charged diatomaceous sediments may contain either a very large amount of oil or a very minor amount of oil. If the amount of oil is large, oil delivery to the reservoir series might have begun very promptly at the first consolidation of the sediments, and continued throughout the compacting, cementing, and deformation of the oil generating series. The final oil residue would be driven out upon recrystallization of the opal into chalcedony. Thus the process of compacting and recrystallization, slow and long-continued, suggests slow and long-continued delivery of oil from the generating series below to the reservoir series above. It is a curious fact that many of the commercial pools of California are concentrated in the clastic sediments above the deformed generating series of organic opal shales, and the two formations are separated by a profound unconformity. Such a condition proves that the driving out of the oil took place long after the siliceous sediments were deposited and even after they were elevated above sea and eroded, and after the reservoir series had been laid down unconformably upon the generating series.

In the cores of the great anticlines of the Santa Maria district, the opal sediments are crushed, deformed, and fractured (see Figs. 10, 11, 12, 13) and these fractures are filled with hydrocarbon residues. The overlying reservoir series are much less disturbed, and bend over the deformed core in a gentle arch.

It appears that the crushing and deforming and recrystallization of the cores has driven out the hydrocarbons into the less disturbed reservoir series above, and that this process was an extremely slow one. And it may well be that it takes several geological periods to get a generating formation cleared of the last dregs of hydrocarbons.

The writer has limited his study to, and deals here only with, biogenesis of oil by diatoms. However, possibly biogenesis by other organisms (colonial algæ—*Elæophyton*) may be the dominant process of oil generation in other types of "mother rock." As Thiessen says,[13] describing *Elæophyton*:—"The cell walls in the living organism are composed largely of oil or oily substances. No theory of chemical changes from cellulosic or mucous substances into an oil or fat is necessary. The oil is such in the living plant."

STANFORD UNIVERSITY,
STANFORD, CALIFORNIA.

[13] "Origin of the Boghead Coals," U. S. Geol. Surv. Prof. Paper 132, p. 130, 1925.

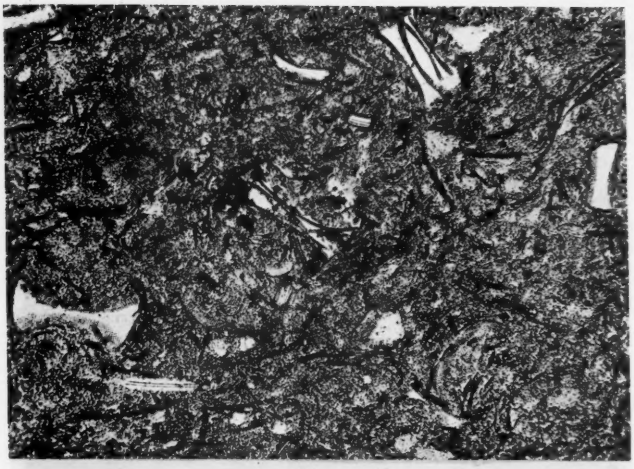

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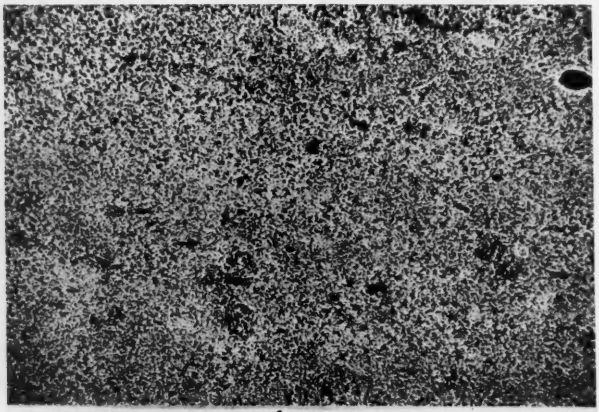
FIG. 2. Photomicrograph (upper nicol out), of pure diatomite, Santa Maria district. The rock is composed of collapsed diatoms, diatom flour, and sponge spicules. The debris composed largely of diatom nobs. × 126.

FIG. 3. Photomicrograph (with upper nicol out), of oil-charged diatomite. The large spot is part of a diatom. The black material on the right is hydro-carbons. Sample is from an oil seep in diatomite where oil has migrated from underlying oil generating shales. × 73.



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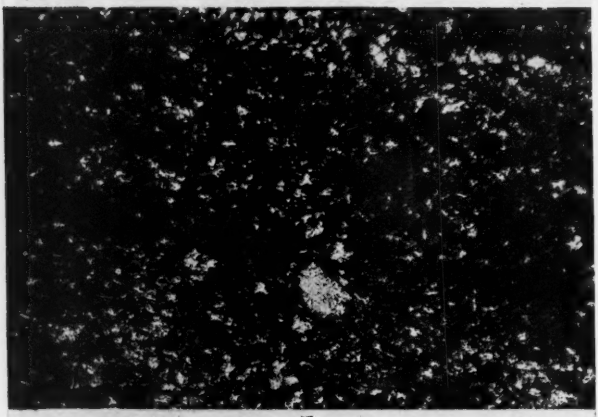

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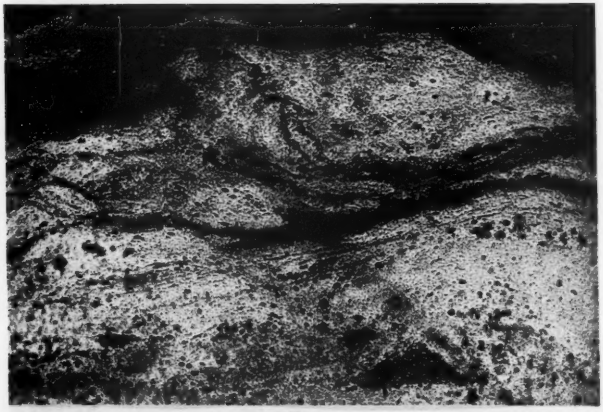
FIG. 4. Photomicrograph (upper nicol out), of dense porcellaneous slabby shales, Monterey formation. The rock is largely opal, with opaque inclusions, minute sponge spicules, and occasional diatoms. × 128.

FIG. 5. Photomicrograph of same field (nicols crossed). White patches show incipient chalcedonization. × 128.



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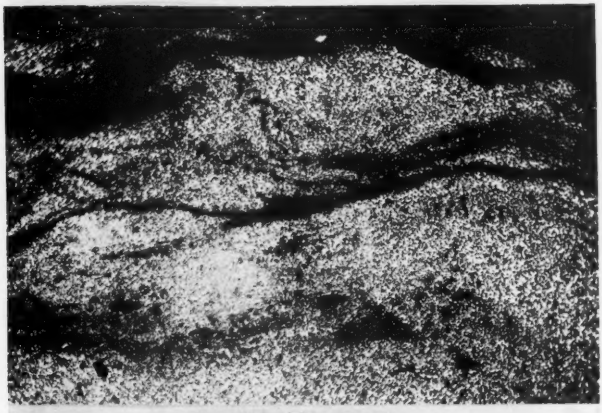

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FIG. 6. Photomicrograph (upper nicol out), of complete chalcedonization of opal, and opaque streaks in same. Dark areas are opaque material and impurities. Light is chalcedony. × 30.

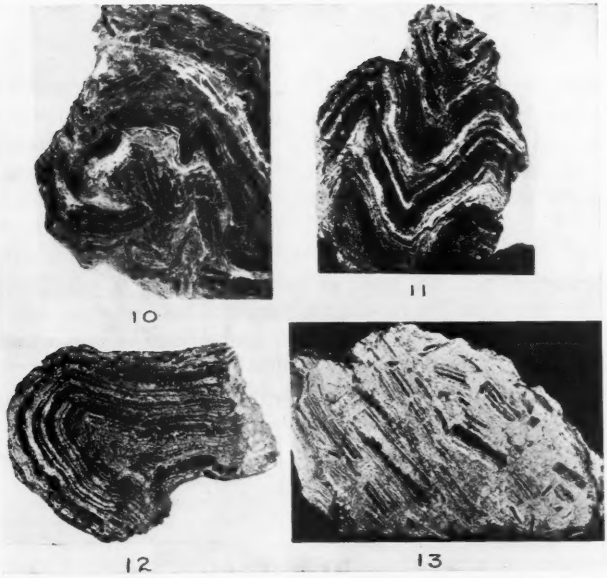
FIG. 7. Same field as Fig. 6 (with nicols crossed). The light colored mosaic is micro-crystalline chalcedony. × 30.

8

9

FIG. 8. Photomicrograph (with upper nicol out) of contorted chalcedonized opal, with opaque streaks, Monterey formation. Black represents opaque impurities of rock; light is chalcedony. × 22.

FIG. 9. Photomicrograph (with crossed nicols). The light gray mosaic is microcrystalline chalcedony. × 22.



FIGS. 10–13. Specimens of banded opal and chalcedony, collected from the central portions of the anticlines of the Santa Maria District. × 1/5 (approx.).

RECENT EVIDENCE CONFIRMING THE ZONAL ARRANGEMENT OF MINERALS IN THE CORNISH LODES.[1]

E. H. DAVISON.

As a result of the work of MacAlister,[2] Cronshaw,[3] Dewey,[4] and the writer,[5] it has been established that the minerals of the Cornish lodes are arranged in a series of zones, one over the other, so that in passing down the lode the predominant metallic minerals vary, and this variation is the same in character throughout the whole district.

The zones are not separated from each other but are "telescoped," that is to say, each zone overlaps the zone above and the one below so that between each pair of typical zones there occurs a zone of intermediate character in which the two neighboring types are blended. Although there are variations in the zones as described by the various authors, the general agreement of the lode systems described is very evident, as will be seen in Table I.

TABLE I.

ZONES OF THE VARIOUS LODES ACCORDING TO DIFFERENT AUTHORS.

MacAlister	Cronshaw	Dewey	Davison
	(9) Calcite	(5) Carbonates of Fe, Mn, etc.	(6) Hematite Siderite Pyrolusite
	(8) Pyrite Hematite Siderite Quartz Fluorite		

[1] Presented before Society of Economic Geologists, Madison, Wis., Dec., 1926.

[2] MacAlister: Geological Survey Memoir, Camborne & Falmouth, 1906.

[3] Cronshaw: "Structure and Genesis of Tin Lodes," etc., *Trans. I. M. M.*, 1921.

[4] Dewey: "The Mineral Zones of Cornwall," *Proc. Geol. Assoc.*, 1925. "Primary Zones of Cornish Lodes," *Geol. Mag.*, 1922.

[5] Davison: "Handbook of Cornish Geology," 1926.

TABLE I.—*Continued.*

MacAlister	Cronshaw	Dewey	Davison
(4) Galena Blende Pyrite Ni, Co, Cu Arsenopyrite Quartz Chlorite	(7) Galena Blende Chalcopyrite Quartz Fluorite	(4) Sulphides of Antimony (3) Sulphides of Pb + Ag giving place at depth to Zn	(5) Galena Blende Pyrite Quartz Dolomite Chalcedony U, Ni, Co
(2) Copper Tin	(6) Chalcopyrite Quartz Fluorite Tourmaline Cassiterite Chlorite (5) Chlorite Tourmaline Cassiterite Arsenopyrite Quartz Fluorite (4) Fluorite Tourmaline Cassiterite Arsenopyrite Quartz Chlorite	(2) Sulphides of Copper + Wolfram + Tin	(4) Chalcopyrite Wolfram Arsenopyrite Quartz Fluorite Pyrite Jasper (3) Chalcopyrite Arsenopyrite Quartz Wolfram Cassiterite Chlorite
(1) Tin	(3) Cassiterite Arsenopyrite Tourmaline Quartz Fluorite (2) Cassiterite Quartz Arsenopyrite Tourmaline (1) Quartz Wolfram Arsenopyrite Cassiterite Feldspar Tourmaline	(1) Oxids of Tin + Wolfram	(2) Cassiterite Arsenopyrite Chlorite + Wolfram near granite cupolas (1) Cassiterite Quartz Tourmaline

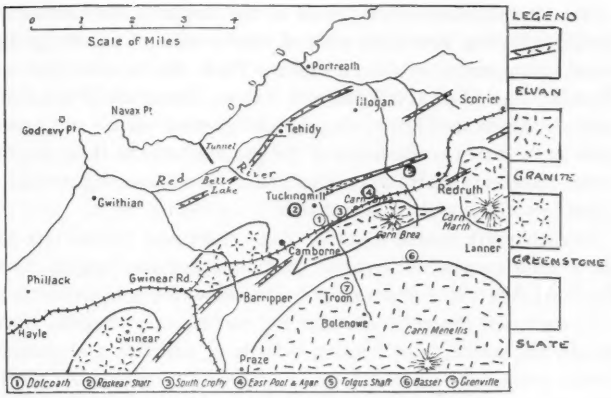


FIG. 1. Map of Camborne District.

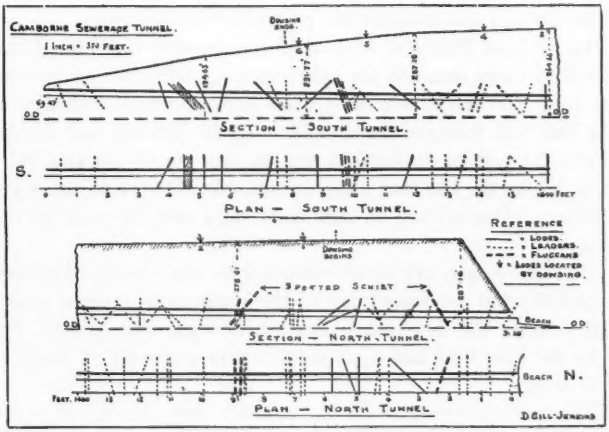


FIG. 2. Sections and plans of the Camborne Sewerage Tunnel.

The three shafts recently sunk to the North of the Camborne Redruth Mining area have yielded new evidence confirming the zonal arrangement of the minerals. These shafts were sunk at Roskear, East Pool and Agar, and Tolgus Mines, which are situated as shown in Fig. 1; they are all vertical shafts and were sunk in the slates to the north of the granite outcrop, their depths being: Roskear shaft, 2,000 feet; East Pool and Agar shaft, 1,400 feet; Tolgus shaft, 2,000 feet.

In each shaft several lodes were cut from near the surface of the ground to near the granite contact, or, in the case of East Pool and Agar, to a depth of 200 feet below the granite contact.

In each case the veins cut near the surface carry galena, zincblende, and pyrite, with fluorite, siderite or ankerite, and quartz. Lower veins carry zincblende and pyrite with no galena but much chlorite; at still deeper levels copper minerals such as chalcopyrite and bornite occur with pyrite and zincblende, the chief gangue minerals being fluorite and chlorite. In the lower veins there is a small proportion of cassiterite but it was not until the shafts began to cut granite or approached the granite contact that the veins showed any considerable proportion of cassiterite.

In the East Pool and Agar shaft the granite was entered at a depth of 1,200 feet, and the lodes carried good values of cassiterite from 100 feet above the granite surface, which improved as the lode was followed downwards. In the Roskear and Tolgus shafts the granite contact has not yet been cut but its proximity is shown by the fact that many granite dikes have been cut in the shafts. At the bottom of each shaft lodes carrying good tin ore occur.

The above facts are in accordance with what would have been expected from our knowledge of the sequence of mineral zones, and confirm the downward sequence of lead, zinc, copper, tin.

In the East Pool and Agar lodes a certain amount of wolfram also occurs.

Another excavation which has recently been carried out in the district is a tunnel through the cliffs to the north of Camborne for drainage purposes. This tunnel was 3,000 feet in length and

for its whole length was in the slates: it cut a number of veins and two faults between which the slate is spotted while on either side of the faults the slates are free from spotting.

This central spotted portion of slate seems to be a horst, and nearer the granite than the slate beyond the faults on either side (Fig. 2). It is significant that it is only in this spotted slate that the lodes carry copper as chalcopyrite and arsenic as arsenopyrite, the lodes in the unspotted slates carrying lead, zinc and pyrite only.

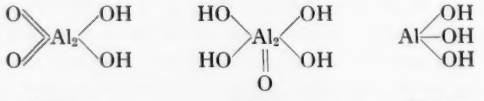
CAMBORNE, CORNWALL,
ENGLAND.

THE ENRICHMENT OF BAUXITE DEPOSITS THROUGH THE ACTIVITY OF MICROÖRGANISMS.

GEORGE A. THIEL.

INTRODUCTION.

THE processes by which aluminous silicates may be converted into hydrates have long attracted the attention of geologists, but they have never been determined with certainty. The field relations of many of the bauxite deposits show clearly that, contrary to what has been commonly assumed, alumina can not be regarded as a static component in rocks and their decomposition products. Three hydroxides occur free in nature, but we have only probabilities as guides to the origin of the solutions from which they were precipitated or the processes by which the silica with which they were associated was liberated. These hydroxides may be represented graphically by assuming that aluminum is a triad as: [1]



Diaspore $Al_2O_2(OH)_2$ | Bauxite $Al_2O(OH)_4$ | Gibbsite $Al(OH)_3$

It is still doubtful whether bauxite exists as a distinct mineral species with the empirical formula $Al_2O_3 \cdot 2H_2O$ as it is commonly designated, for its composition ranges between that of diaspore and gibbsite. It is perhaps simply a mixture of the two hydrates in an amorphous state.[2] Furthermore from its widely varying geologic modes of occurrence, it is evident that a general explanation for its accumulation and enrichment can not apply to

[1] Mellor, J. W., "Modern Inorganic Chemistry." Longmans and Co., London, 1920.

[2] Clarke, F. W., 'Data of Geochemistry," U. S. Geol. Survey Bull. 770, 1925.

each type of deposit. Nevertheless, a résumé of the literature dealing with the bauxite and laterite deposits on all of the continents, indicates that the solution and re-precipitation of aluminum at some distance below the surface is a prominent factor in the formation of many large bodies of high-grade bauxite ore.

The results of a series of experiments dealing with organisms that are commonly active near the surface in the zone of leaching, lead the writer to conclude that more aluminum is liberated from the silicates in the mantle rock waste than average analyses of meteoric ground waters would indicate. Its precipitation may occur in place almost contemporaneously with the formation of the aluminous solutions, yielding new silicates including kaolinite,[3] or if in a colloidal state the alumina may be transported to a considerable depth before coagulation occurs.

EVIDENCE OF SECONDARY ENRICHMENT.

In most of the bauxite districts of the world there is some evidence of secondary enrichment within the ore body itself, such as contraction cracks filled by later addition of aluminum hydrates carried in solution, or the pisolitic structures within the ore, interpreted to denote the migration of dissolved alumina. However, a more striking characteristic of most bauxite deposits is the presence of a siliceous or ferruginous overburden capping the ore. In some cases mechanical erosion has removed the greater portion of such residual debris, exposing the bauxite at different levels in the ore body.

In Alabama and Georgia many of the ore bodies were originally covered to a depth of from 3 to 6 feet with a bright yellow siliceous residual clay, containing an appreciable amount of chert.[4] The Maddax Bank and the Watters Bank in Floyd County, Georgia, are typical examples. In Bortow County of the same state the ore body is covered by a deep red residual cherty clay, derived from limestone and the included chert.[5]

[3] Schwarz, R., "Über das Problem der Kaolinbildung," *Tonnindustrie Zeitung*, 1924.

[4] Watson, T. L., "Bauxite Deposits of Georgia," Geol. Survey of Georgia, Bull. 11, p. 73, 1904.

[5] Watson, T. L., *loc. cit.*

At a number of localities in British Guiana the bauxite beds are derived from a porphyrite or tuff. Alteration has produced a surface soil over the aluminum ore that is a sand varying from white, glistening, almost pure quartz, to a brownish, highly arenaceous soil. The subsoil contains less quartz—from 20 to 45 per cent.—and a high proportion of free alumina. This is underlain by a thick deposit of cream colored bauxite more or less stained with iron, and with buff colored arenaceous clay.[6]

In India the bauxite laterites cap basic trap and from the intimate relationship between kaolin, kaolinized trap, and bauxite, any theory for a later sedimentary origin for the clays and ores is untenable. By hydration and kaolinization the trap has been converted into laterite, and by selective segregation a zone of enriched aluminum hydroxide has been formed below a highly ferruginous cap. In publishing hints for searching for bauxite the India Geological Survey states:[7] "Flat hills are usually the highest land in the trap areas. On these flat-topped laterite-capped hills the best places to search are the scarps and invariably the top ten feet of the scarps. It is a common feature to find that the very top is made up of the iron variety, but just under this covering the best gray bauxite occurs."

Near the village of Kaliwada, India, is a typical case. The upper 100 feet of several of the hills consists of mottled purplish and white clayey trap which passes up without any sudden change into a compact lateritoid mass. In a pit on one of these hills a clear section shows the secondarily enriched bauxite zone. The upper 4 feet consists of hard, nodular, ferruginous laterite, followed by 3 to 5 feet of excellent gray pisolitic bauxite. This passes down into pink and brick colored, vermicular laterite.[8]

The bauxite deposits of Arkansas derived from a nepheline syenite rock, show a marked downward secondary enrichment of alumina.[9] The top 3 to 5 feet of the ore contains nearly three

[6] Harrison, J. B., "'Laterite' in British Guiana," *Geol. Mag.*, vol. 47, p. 440, 1910.

[7] Fox, C. S., Memoir Geological Survey India, vol. XLIX, Pt. 2, 1923.

[8] Fox, C. S., *op. cit.*

[9] Mead, W. J., "Bauxite Deposits of Arkansas," ECON. GEOL., vol. 10, p. 28, 1915.

times as much silica as the main mass of the ore body. Table I. gives a series of analyses showing a pronounced increase of alumina with depth.

TABLE I.

SHOWING SILICA-ALUMINA RATIOS AT VARIOUS DEPTHS IN THE ARKANSAS BAUXITE DEPOSITS.[10]

Depth.	SiO_2.	Al_2O_3.
3 ft.– 5 ft.	24.85	46.04
5 ft.– 7 ft.	13.54	54.30
8 ft.– 9 ft.	14.63	52.41
9 ft.–11 ft.	7.73	57.98
11 ft.–13 ft.	9.96	56.41
13 ft.–15 ft.	9.65	57.16
15 ft.–17 ft.	9.00	56.76

Mead is of the opinion that the downward secondary concentration of the alumina is due to the solubility of bauxite in surface solutions, leaving kaolin and hence the silica in a relatively higher percentage at the surface. Experimental work indicates, however, that under some conditions alumina may be extracted from the kaolin (see Fig. 2) leaving a siliceous residue as found over many bauxite deposits.

THE SOLUBLE ALUMINA IN RESIDUAL ROCK.

The amount of soluble alumina has been determined for many soils, residual clays and natural waters.[11] Hilgard found in soils an excess of aluminum above that required to combine with the silica to form kaolinite, and therefore concluded aluminum hydroxide was present.[12] Edwards calculated from the recorded analyses of over 200 clays from various parts of the United States that most of them contained a higher ratio of alumina to combined silica than that required for the formation of kaolin. He likewise concluded that hydrous aluminum oxides must be present.[13] Silica, alumina, water ratios as determined by analyses

[10] From table of analyses by Mead, *loc. cit.*

[11] See Clarke, F. W., "Data of Geochemistry," U. S. Geol. Survey Bull. 770, 1925.

[12] Hilgard, E. W., "Soils." Macmillan Co., New York, 1914.

[13] Edwards, M. G., "The Occurrence of Aluminum Hydrates in Clays," ECON. GEOL., vol. 9, 1914.

are not in themselves sufficient proof of the presence of kaolin, for the silica and alumina may not be combined as silicates, but rather as hydrous silica and colloidal alumina in such amounts as to give a ratio similar to that of kaolinite.[14]

The exceedingly small amounts of alumina present in most natural waters is undoubtedly due to the fact that amounts of soluble hydrates greater than a few parts per million can exist only when the reaction is more acid than pH 4.7 or more alkaline than about pH 8.0.[15] However, the amount that can be held in solution is markedly increased when the reaction becomes more acid or more alkaline. (See solubility curve, Fig. 1.) Banerji [16] found pH 6.7 as the iso-electric point of aluminum hydroxide, at reactions more alkaline or acid it re-dissolved.

Some organic acids tend to prevent the precipitation of aluminum under slightly acid conditions, and it might therefore be contended that the organic acids near the surface would form considerable amounts of aluminum salts which would be carried to the depth where bauxite ores are enriched. For example, 200 parts per million of aluminum acetate in water at ordinary temperatures will not be precipitated at pH 5.4 even on prolonged standing.[17] The presence of such simple organic acids as formic, acetic, and propionic has been demonstrated by many investigators,[18] but it is doubtful whether any great amounts of the acids can exist in the soil for any length of time, as they are vigorously attacked by bacteria and molds and oxidized to CO_2 and water.[19] The resulting carbonated waters may aid in the leaching of silica, but their effect on the solution of alumina is negligible.

A high percentage of the total colloids in residual clays is composed of aluminum, but in most cases it is associated with col-

[14] Ries, H., Discussion. ECON. GEOL., vol. 9, 1914.

[15] Magistad, O. C., "The Aluminum Content of the Soil Solution," *Soil Science*, vol. 20, p. 181, 1925.

[16] Banerji, *Indian Med. Res.*, vol. 11, p. 695, 1924.

[17] Magistad, O. C., *op. cit.*, p. 196.

[18] Van Hise, C. R., "Treatise on Metamorphism," U. S. Geol. Survey, Mon. 47.

[19] Kröber, E., *Jour. Landw.*, vol. 57, p. 5, 1909. Pierre, I., *Compt. Rend. Acad. Sci.* (Paris), vol. 59, p. 286. Staklasa, J., *Biochem. Zeitsch.*, vol. 91, p. 137.

loidal silica in amounts near the ratio in which the two elements combine to form kaolinite. The colloids extracted from 44 different residual clays representative of various localities and climatic conditions, on analysis showed that the colloidal material

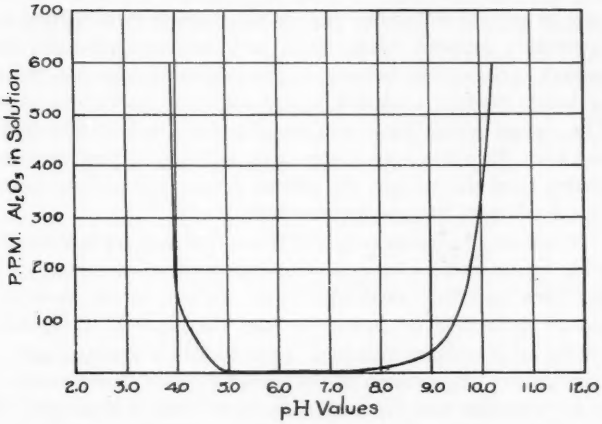


FIG. 1. Curve showing the parts per million of Al_2O_3 in solutions from soils in which the reaction had been changed by the addition of H_2SO_4 or NaOH. Modified from Magistad, O.C. in *op. cit.* pH = Log. 1/Hydrogen-ion Concentration.

is mainly composed of silica, alumina, iron oxide and water. Silica varied from 31 to 55 per cent., alumina from 16 to 38, iron oxide from 4.6 to 16.4, and water from 3.3 to 16.5.[20] In cases where the alumina was high the silica was surprisingly low, whereas iron showed no consistent relation to the other two major constituents. The presence of a high colloidal alumina-silica ratio in some clays is indicative of the process which, when in operation for an extended period of time, leads to the enrichment of bauxitic clays at depth.

[20] Davis, R. O. E., "The Nature of Soil Compounds and their Relations to Sedimentation," Researches in Sedimentation, 1924, Nat. Res. Council, Washington, 1925.

Not all of the aluminum liberated from kaolinite remains in the clay as the readily soluble hydroxides. The presence of zeolites (basic hydrated aluminum silicates) indicates that where alkaline solutions are active, sodium silicate and sodium aluminate combine to form zeolites. The steps in zeolite formation may be outlined as follows: sodium carbonate is formed from the interaction between white alkali and calcium carbonate; the sodium carbonate hydrolyzes to give sodium hydroxide, which ionizes to produce a solution of high alkalinity (pH 10 to 11.5). The sodium in turn forms sodium silicate and sodium aluminate, and when the pH is lowered due to the addition of fresh meteoric waters from the surface, the sodium silicate and sodium aluminate combine to form sodium zeolite.[21]

In regions of alkaline rocks the above reactions are indoubtedly a big factor in the solution and re-deposition of alumina, for it has been definitely established that sodium zeolite produces sodium hydroxide by hydrolysis and the latter is a vigorous solvent of aluminum silicates. (See solubility curve, Fig. 1.) Furthermore, the solution of the aluminates that do not combine to form zeolites also yields alkaline waters due to hydrolysis, as shown in the following equation:[22]

$$NaAlO_2 + 2H_2O \rightleftarrows NaOH + Al(OH)_3.$$

In such an event more sodium hydroxide is liberated and the alumina is carried away as a hydrate.

Aluminum silicates are also readily attacked by solutions of nitric, hydrochloric and sulphuric acids. It is probable that in most cases the formation of acid solutions by the oxidation of pyrite or other iron sulphides is the first step in the alteration of residual clays or shales and the solution of alumina. This solution of alumina would of course be accompanied by a liberation of silica in a colloidal or finely divided form which would dissolve more readily when it encountered alkaline solutions and

[21] Burgess, P. S. et al., "Zeolite formation." *Science*, n. s., vol. LXIV., p. 625, 1926.

[22] McGeorge, W. T. et al., "Aluminum Hydroxide and the 'Freezing Up' of Alkali Soils, etc." *Science*, n.s., vol. LXIV., 1926.

thus be removed. The presence of colloidal iron sulphide does not cause precipitation of silica and consequently the silica once liberated would be carried beyond the region of oxidation and acid formation.

The results of experimental work by the writer dealing with various groups of ammonifying and sulphate reducing bacteria that are commonly present near the surface in residual soils and rock waste, indicate that through the aid of biochemical reactions there is a conservation of essential constituents, and a very small amount of iron sulphate is sufficient to produce the liberation of relatively large quantities of alumina.

LEACHING EXPERIMENTS.

Experiment 1. Materials and Methods.

The following samples of clays and shales were employed in the leaching experiments:

A. Decorah shale from an exposure along the valley of the Mississippi river at Cherokee Heights, St. Paul, Minnesota.
B. Kaolinite, C.P. Chemical Supply Company stock preparation.
C. Kaolinite to which was added one fourth volume magnesite C.P.
D. White kaolin from a blanket deposit in Cambrian dolomites in the Black Hills near Lead, South Dakota.
E. White clay from the Cretaceous sediments associated with bauxite deposits in southeastern Alabama.
F. Fresh, finely-ground microcline from large crystals in a pegmatite in northeastern Minnesota.

The clays were crushed to pass an 80-mesh screen and equal amounts were placed in 500 c.c. flasks each fitted with a drain and stopcock at the lower margin to allow the leaching solutions to percolate through the clay and drain into a container. A stock supply of solution was prepared to insure uniformity of composition for the whole series. It consisted of natural spring water from a spring issuing at the base of the glacial drift, to which was added 100 c.c. per liter of a filtered extract washed from the black mud in the pool of the spring. The extract was added to insure the presence of organic constituents for bacterial

growth. All of the solution was sterilized in an autoclave at 20 pounds pressure for twenty-five minutes.

Two sets of leaching experiments were arranged as follows:

Group I.—The clays were saturated with the stock solution and inoculated with 5 c.c. of a culture solution containing active sulphate-reducing bacteria.[23] Since these organisms thrive most actively under partially anaërobic conditions, the bottom stopcocks were closed and the flasks stoppered for five days to allow the bacteria to multiply and permeate the wet clay. By the end

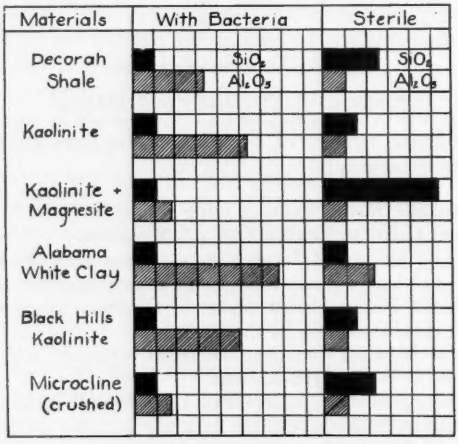


FIG. 2. Showing graphically the ratio of silica and alumina taken into solution by the leaching of clays.

of the fifth day minute black specks of iron sulphide began to appear in the clay. The flasks were then opened and the spring

[23] For the growth of a stock supply of sulphate reducing organisms the following culture solution was prepared:

Iron lactate	5.0 grams
Ammonium sulphate	2.0
Diabasic potassium phosphate	0.5
Distilled water	1000.0

water was added a drop at a time by means of a siphon. The solutions penetrated the clay and the leachings dripped through a filter into a container.

Group II.—The apparatus and material of Group I was duplicated but not inoculated with bacteria. All glassware and materials were sterilized. The same procedure was followed as in the first experiment, but the flasks were plugged with dry cotton stoppers to prevent contamination.

The leachings from each of the flasks were evaporated and the amount of silica and alumina in the residue determined. The resulting silica-alumina ratios are represented graphically in Fig. 2.

Experiment 2. In order to determine the effect of organisms that are active in the mantle rock, on the solubility of aluminum silicates near the surface, a leaching experiment was so arranged as to allow access to atmospheric conditions. A large glass funnel 16 inches in depth was coated with paraffin on the inside to prevent the solutions from coming in direct contact with the silica of the glass. Finely ground kaolinite was placed in the apex of the funnel to a depth of about 6 inches and the remaining portion filled with loamy glacial soil. The soil was moistened with a culture solution containing sulphate reducing organisms to insure the presence of that group of bacteria. Spring water from the glacial drift, to which was added 100 c.c. per liter of a filtered extract from black pond mud, was allowed to percolate slowly through the soil and underlying kaolinite in the funnel. One liter of leaching was caught in a flask as it dripped from the funnel and upon evaporation the residue contained 5.31 parts of Al_2O_3 to 1 part of SiO_2. A microscopic examination of the residue showed that a large proportion gave optical properties corresponding to the ferro-aluminum sulphate, halotrichite, undoubtedly some aluminum sulphate and ferrous sulphate were also present, but in smaller amounts.

The above experiment was duplicated using some of the same natural waters, but with all apparatus and materials sterilized. It is obvious that the material in an open funnel would not remain

perfectly sterile for an extended period of time, but only air and dust contaminating organisms could gain access. In this case the residue collected as indicated above, contained 1.37 parts SiO_2 to 1 part of Al_2O_3.

TABLE II.

SHOWING THE RELATIVE SOLUBILITY OF SILICA AND ALUMINA IN THE PRESENCE AND IN THE ABSENCE OF BACTERIAL ACTIVITY. (EXPERIMENT 2.)

With bacteria	5.31 parts Al_2O_3 to 1 part SiO_2
Sterile	1.37 parts Al_2O_3 to 1 part SiO_2

DISCUSSION.

By comparing the results plotted in Figure 2 it is evident that biochemical reactions are instrumental in liberating a far greater amount of alumina than that taken into solution by sterile natural waters. Undoubtedly the most active agent in dissolving the alumina is the sulphuric acid generated by the oxidation of freshly precipitated colloidal iron sulphide by bacterial activity. The source of iron and sulphur may not appear adequate in the field, but in this connection it should be recalled that most bauxite deposits are stained with iron, and that colloidal sulphur is a common constituent in most surface soils. The presence of conspicuous pyrite nodules or finely disseminated megascopic grains of pyrite are not required to yield sufficient acid to leach the alumina from its silicate compounds. A comparatively small amount is sufficient to initiate a process which when once started conserves its resources by passing through cyclic reactions. These reactions can take place at a few feet below the surface, for sulphate reducing organisms thrive at a depth of a few inches in the residual soils. They have the power of taking oxygen away from sulphates, sulphites or thiosulphates and reducing them to sulphides. If these compounds happen to contain iron, ferrous sulphide is formed directly. In the experiments described above, its presence was detected as minute black specks in the white clay.

In the solution and migration of alumina through the aid of bacterial activity, the following reactions are perhaps instrumental in bringing about its solution and re-deposition at greater depths:

(1) $$FeS_2 + H_2O + 7O = FeSO_4 + H_2SO_4.$$

The resulting acid would attack the aluminum minerals yielding an aluminum sulphate solution:

(2) $$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + H_2SO_4 = Al_2(SO_4)_3 \cdot H_2O + SiO_2 \cdot H_2O + H_2O.$$

In aqueous solution the sulphate is hydrolyzed, yielding aluminum hydrate:

(3) $$Al_2(SO_4)_3 + 6H_2O = 2Al(OH)_3 + 3H_2SO_4.$$

Iron may enter into combination with the aluminum sulphate to form a series of double sulphates or pseudo-alums (such as $Al_2(SO_4)_3 \cdot FeSO_4 \cdot 24H_2O$, which occurs as the mineral halotrichite) or it may form the hydrous sulphate melanterite ($FeSO_4 \cdot H_2O$).[24] All of these sulphates are readily soluble in cold meteoric waters, and it is probable that their solutions are soon hydrolized to liberate more free acid. Ferrous sulphate is readily oxidized to ferric sulphate and this subsequently breaks down liberating sulphuric acid and ferric hydroxide. From the solubility curve of alumina, as shown in Fig. 1, it is obvious that the aluminum sulphate would not remain in solution sufficiently long to carry the sulphate radical very far from its source. In fact the separation indicated in reaction 3 might occur in place almost contemporaneously with the formation of the sulphate solution.

In the synthetic production of pyrite[25] under vadose conditions, it has been found that its precipitation is favored or induced by aluminous material, or by fine slimes in a reducing environment. In the reactions listed above the "reducing environment" is produced by bacterial growth. There is an abundance of field evidence indicating that the natural reduction of sulphates through biochemical processes is in progress under a great variety of con-

[24] Logan, W. N., "Kaolin in Indiana," Dept. of Conserv. Indiana, Pub. 6, 1919.

[25] Whitman, A. R., "The Vadose Synthesis of Pyrites," ECON. GEOL., vol. 8, p. 455, 1913.

ditions both near the surface and at great depths.[26] The presence of hydrogen sulphide in many of the wells and springs in the Cretaceous sediments in the bauxite districts of Georgia and Alabama denotes the reduction of conate waters at some distance below the surface at the present time. The same reaction is also in progress in the Cretaceous sediments of northwestern Minnesota.[27]

It might be contended that the oxidation of sulphur and pyrite initiated by biochemical process would lead to the development of toxic solutions in which bacteria could not continue to thrive. Experimental work has shown, however, that some of these bacteria continue to live in a more acid medium than any other living organism yet reported, the hydrogen-ion concentration of the medium increasing to a pH 0.6 and less.[28] Solutions with that pH value are capable of holding appreciable amounts of alumina in solution (See Fig. 1). Furthermore, the influence of aluminum as a toxin to surface organisms does not appear to be important,[29] in fact aluminum salts are stimulating to the ammonifying organisms.

By comparing the experimental results shown in Fig 2 it is evident that the alumina is in a more stable form in some clays than in others. However, such variations are to be expected, for a study of the products of rock weathering has quite conclusively demonstrated that the colloidal material due to the weathering of silicates commonly consists of separated silica and alumina, rather than silicates of aluminum, and that in a state of mutual adsorption these two constituents form a mixture that is very near that of a colloidal silicate of aluminum.[30] Most clays contain varying amounts of such amorphous colloidal oxides, and

[26] Bastin, E. S., "The Problem of the Natural Reduction of Sulphates," *Bull. Am. Assoc. Petrol. Geol.*, vol. X., 1926. Thiel, G. A., "Manganese Precipitated by Microörganisms," ECON. GEOL., vol. 20, p. 301, 1925.

[27] Allison, I. S., personal communication.

[28] Wakeman and Joffe, "Microörganisms Concerned in the Oxidation of Sulphur, etc.," *Jour. Bact.*, vol. VII., No. 2, 1922.

[29] Whiting, A. L., "Inorganic Substances, Especially Aluminum, in Relation to the Activity of Soil Microörganisms," *Jour. Am. Assoc. of Agrom.*, vol. 15, 1923.

[30] Stremme, J., Doelter's "Handbuch der Mineralchemie," Bd. II., p. 30, 1917.

since they are more unstable than the silicates they are more readily leached. The microcline, as shown in Fig. 2, was introduced to compare the silica-alumina ratio, leached from residual clays, with that of fresh aluminum silicate containing no colloidal material. The amount of alumina taken into solution in the presence of biochemical reactions is greater than that of silica, but the ratio is much lower than for any of the clayey products of weathering.

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MINERAL DEPOSITS OF THE HYDER DISTRICT, SOUTHEASTERN ALASKA.

W. B. JEWELL.

INTRODUCTION.

DURING the summer of 1925, from July 11th to September 20th, the writer served as assistant to A. F. Buddington in a study, for the U. S. Geological Survey, of the mineral deposits and geology of the Salmon River section of the Hyder district at the head of Portland Canal in Southeastern Alaska. The data secured in the field at that time, combined with a subsequent intensive microscopic study of the ores in the laboratory, form the basis for the following article.

The data consist of field observations on 125 separate veins and the results of laboratory work on 250 polished sections, 219 of which are from deposits in the Salmon River section of the Hyder mining district. The remaining sections are from the adjoining area in British Columbia.

It is thought that the present paper may prove of interest because of the similarity and the close proximity of these deposits to those on the Canadian side which have come into prominence because of the extraordinary richness of the ores of the Premier mine.

It is realized that the conclusions drawn are not final and may have to be revised when additional work is done in the region, but it is believed that quantitatively the data are sufficient to point to quite definite conclusions.

The laboratory work was done in the Department of Geology of Princeton University. The writer is under great obligation to Professor A. F. Buddington, and is also highly indebted to other members of the Department, especially Professors C. H. Smyth, Jr., Edward Sampson, and A. H. Phillips.

GENERAL GEOLOGY.

A description of the general geology of a portion of the district has been published by Westgate.[1] Buddington [2] has recently published a summary which contains excellent descriptions of the general geology and structure. The geology of the adjacent Canadian territory has been ably described by Schofield and Hanson.[3] The description of the general geology of the region is here summarized from these publications.

The bedded rocks of the area consist largely of tuffaceous graywacke, argillite, slate, and volcanic tuffs with which are intercalated rare quartzite and limestone beds and, locally, considerably altered andesitic flows. This series is undoubtedly the equivalent of the Bear River and Nass formations described by Schofield and Hanson in the adjacent Canadian territory. Hanson [4] in a later publication correlates these rocks with the Hazelton group to the south, which is of probable Jurassic age. This series in the Salmon River area has been sharply folded. Many of the folds are isoclinal, and some are overturned to the southwest. The axes of the folds are in general parallel to the trend of the main batholith in the area.

The sediments and volcanics are intruded by the Texas granodiorite batholith, in which the stratified rocks occur as isolated roof fragments over much of the area. The name "Texas granodiorite" is proposed by Buddington.[5] This granodiorite is porphyritic and in places contains phenocrysts of potassic feldspar up to three fourths of an inch long. Dikes and tongues of this granodiorite extend into the bedded rocks, and frequently mineral deposits are related to these offshoots. The Texas

[1] Westgate, L. G., "Ore Deposits of the Salmon River District, Portland Canal Region," U. S. G. S. Bull. 722, pp. 117–140, 1920.

[2] Buddington, A. F., "Geology and Mineral Deposits of the Salmon River Area, Southeastern Alaska," *Eng. & Min. Jour.*, Mar. 26, 1927.

[3] Schofield, S. J., and Hanson, George, "Geology and Ore Deposits of the Salmon River District, B. C.," Can. Geol. Survey Mem. 132, 1922.

[4] Hanson, George, "Reconnaissance between Skeena River and Stewart, B. C.," Canadian Geol. Survey, Summary Report, Part A, pp. 32–36, 1923.

[5] Buddington, A. F., *op. cit.*

granodiorite, which is probably the equivalent of the Premier porphyry sills of Schofield and Hanson, is highly altered in places to chlorite, epidote, and zoisite. Much of it shows a primary gneissic structure.

The Texas granodiorite, the sediments and volcanics, and the mineral deposits, are all cut by the quartz monzonite, granodiorite, and dikes related to these intrusives, of the main Coast Range batholith. This great batholith extends to the west for from 40 to 50 miles in this latitude and for hundreds of miles to the north and south. The dominant rock of the eastern edge of the Coast Range batholith, along which the Salmon River area lies, is quartz monzonite. The outlying stocks and dikes related to it are generally granodiorite, quartz diorite, or diorite. The dikes vary in width from a few feet to many hundreds of feet and occasionally show dark, dense, chilled border phases. The younger intrusives have a fresh pinkish appearance in contrast to the waxy gray of the older Texas. A series of dark, dense hornblende lamprophyres and malchite dikes occur cutting all other rocks exposed in the area as well as the veins.

All the veins of importance, practically without exception, occur within 1,500 feet of the Texas-Hazelton Group contact, while a large majority of them occur within a few hundred feet of the contact and many directly at it. Moreover, many of the deposits in the bedded rocks were found to be closely associated with tongues and dikes of the Texas intrusives. A marked grouping of such a large number of veins along the contact, together with the fact that the diorite and granodiorite dikes related to the quartz monzonites and granodiorites of the main batholith cut the ore veins, can mean but one thing, namely, that the deposits are not related to the main Coast Range intrusives in origin, but to an earlier granodiorite which is quite different from them. The unimportant veins related to the quartz monzonite bear no similarity to the deposits in question. They are chiefly glassy quartz veins carrying pyrite, principally, with smaller amounts of magnetite, specularite, and molybdenite. The minerals tetrahedrite, galena, sphalerite, and chalcopyrite that are so characteristic of

the Texas veins are conspicuously absent. The lamprophyric rocks are also sometimes mineralized with pyrite, but no other ore mineral was observed in them.

Most of the veins occur in the Texas granodiorite and in the greenstones and tuffaceous graywackes. A few occur in the argillites and slates, but they are much less abundant than those in the more massive and brittle rocks. Of the total 87 veins that have been studied in detail, two thirds are in the sediments and volcanics, one sixth at or very close to the Texas-Hazelton Group contact, and one sixth well within the Texas batholith. Of the veins in the bedded rocks, 42 per cent. occur in the greenstones, the remaining 58 per cent. in other members of the Hazelton Group but principally in the tuffaceous graywackes.

MINERAL DEPOSITS.

The mineral deposits of the district include a number of different types. Fissure veins, disseminated replacement deposits (principally in greenstone), and mineralized shatter and shear zones occur. The veins in the Texas batholith are practically all fissure veins characterized by the predominance of quartz as a gangue and pyrite and galena as ore minerals. Fissure veins in the bedded rocks are not so numerous as in the granodiorite, and disseminated replacement and mineralized shatter and shear zone types are most common. Arsenopyrite, pyrrhotite, and sphalerite occur in greater quantities in the roof rocks, whereas galena, though still present, is relatively less abundant. Most of the deposits in the Hazelton series are of the base metal type with generally low, though erratic, values in gold and silver. The ore in the veins within the granodiorite is generally in the form of massive shoots that often contain high values in gold or silver or both.

Character of the Ore.—The ore minerals are principally pyrite, galena, sphalerite, and chalcopyrite, with locally large amounts of arsenopyrite, pyrrhotite, and tetrahedrite. Economically, gold is an important mineral. The ore is generally massive and shows a definite paragenesis of the minerals.

Many of the moderately argentiferous lead veins of this district carry an unusually high gold content for this type of mineralization. The concentrates from the Riverside mine in 1926 are reported by Mr. Mellin, the consulting engineer in charge, to have contained per ton: 1.4 oz. in gold, 33.14 oz. in silver, and 62 per cent. lead. Some of the ore is gneissic, and the veins in which it occurs show slickensided walls, gouge, or other evidences of movement. Steel galena is much more abundant in these veins than in those that show no such evidences. The gneissic ore, which consists of elongated bands of brecciated pyrite, sphalerite, pyrrhotite and other sulphides in gneissic galena, resembles very closely the ores of the Slocan District, British Columbia, as described by Uglow [6] and later by Bateman,[7] the veins of the Cœur d'Alene district described by Waldschmidt,[8] and similar banded ores described by Emmons [9] and by Lindgren and Irving.[10] This type of ore, in which the banded structure is largely due to the orientation of the galena cleavage, is, however, not abundant in the Hyder district.

Alteration of Country Rock.—The country rocks adjacent to the veins are often impregnated with pyrite for considerable distances, and are locally altered to quartz, chlorite, and sericite. In the sediments and volcanics, carbonates are an important alteration product in the wall rock.

Relation to Topography.—Difference in elevation has no effect on the character or content of the veins. The same sulphides occur alike in the veins below sea level and those up to 5,000 feet and over. It therefore seems probable that the deposits were precipitated at depths where a few thousands of feet of cover more

[6] Uglow, W. L., "Gneissic Galena Ore from the Slocan District, B. C.," Econ. Geol., vol. 12, pp. 643–662, 1917.

[7] Bateman, A. M., "Silver-Lead Deposits of Slocan District, B. C.," Econ. Geol., vol. 20, pp. 554–572, 1925.

[8] Waldschmidt, W. A., "Deformation in Ores, Cœur d'Alene District, Idaho." Econ. Geol., vol. 20, pp. 573–586, 1925.

[9] Emmons, W. H., "Some Regionally Metamorphosed Ore Deposits and So-called Segregated Veins," Econ. Geol., vol. 4, pp. 755–781, 1909.

[10] Lindgren, Waldemar, and Irving, J. D., "The Origin of the Rammelsberg Ore Deposit," Econ. Geol., vol. 6, pp. 303–313, 1911.

or less made no difference either in the minerals deposited or in their relative abundance. The proximity to the Texas-Hazelton contact and the type of country rock seem to be the sole factors in determining the position of the deposits.

Zonal Distribution.—The zoning that ore deposits exhibit outward from their source of origin has been noted again and again in mining camps, and has lately come to be regarded as a fundamental law. The mineral deposits of the Hyder district are anomalous in this respect. They apparently present peculiar reversals of zoning. As the data are based on 219 polished sections taken from 87 different veins and the field study of 125 veins, it is thought that these anomalies are real and that they are not due to insufficient data.

TABLE I.

MINERAL DISTRIBUTION IN THE 87 VEINS STUDIED IN DETAIL.

		Per Cent.
Quartz	occurs in	90
Chalcopyrite	" "	84
Pyrite	" "	80
Galena	" "	80
Sphalerite	" "	78
Pyrrhotite	" "	45
Tetrahedrite	" "	38
Calcite	" "	31
Barite	" "	21
Arsenopyrite	" "	16
Anisotropic intergrowth	" "	7
Freibergite	" "	6
Strongly anisotropic grains	" "	6
Scheelite, Ankerite, Strongly anisotropic spikes, Bright white blebs, Bluish white blebs, Molybdenite, Chalmersite, Gold, Proustite	occur in less than	5

In Table I. the figures represent the percentage of the 87 veins in which the mineral occurs. These figures, though they do little

more than suggest absolute quantities, give a fair idea of the relative distribution of the various minerals, and show very strikingly that the typical vein of the district is essentially composed of pyrite, galena, sphalerite, and chalcopyrite in a quartz gangue.

In Table II. the more abundant ore minerals and gangues are arranged according to their distribution in three groups of veins; namely, veins well within the Texas batholith, veins close to or at the Texas-Hazelton Group contact, and veins in the sediments and volcanics of the Hazelton Group.

TABLE II.

DISTRIBUTION OF THE ABUNDANT ORE MINERALS AND GANGUES IN THREE VEIN GROUPS.

		(1) %	(2) %	(3) %
Pyrite	occurs in	86	86	78
Galena	" "	93	93	75
Chalcopyrite	" "	93	76	83
Sphalerite	" "	79	71	80
Tetrahedrite-Freibergite	" "	50	64	37
Pyrrhotite	" "	29	29	53
Arsenopyrite	" "	0	7	22
Quartz	" "	100	100	85
Calcite	" "	0	7	44
Barite	" "	43	29	14

(1) Veins well within the Texas batholith.

(2) Veins close to or at the Texas-Hazelton contact.

(3) Veins in the sediments and volcanics of the Hazelton Group.

The above Table II. shows a very definite zoning, but one which is the reverse in many respects from that which might be expected from current theories. The usual zoning in primary metalliferous deposits is a tendency for the minerals that crystallize under relatively high temperatures and pressures to occur nearer the source of supply, while those that crystallize under lower temperatures and pressures occur in shells or zones farther away from the parent rock. In the Hyder district, the higher temperature minerals, *e.g.*, arsenopyrite, pyrrhotite, and sphalerite, occur more abundantly in the roof rocks; while the supposedly lower temperature minerals, *e.g.*, galena, tetrahedrite, and other silver-bearing minerals, are more abundant in the granodiorite.

A glance at Table II. will show that pyrite, galena, chalcopyrite, tetrahedrite, quartz, and barite are more abundant in the granodiorite; whereas sphalerate, and especially pyrrhotite, arsenopyrite, and calcite, are more abundant in the overlying sediments and volcanics. The great development of pyrrhotite in the roof rocks may perhaps be explained by its apparent affinity for the greenstones, and to a lesser extent for the dark basic graywacke; but no similar explanation seems available for the relations of galena, tetrahedrite, barite, arsenopyrite, and sphalerite.

Bateman notes that in the Slocan district of British Columbia the silver values are higher in the veins in the granodiorite, while veins in the roof rocks are characterized by a higher percentage of galena, sphalerite, and siderite, and by decreasing amounts of quartz. He says:[11]

> The ores in the granodiorite (type 1) are highly siliceous, zinc is scarce, lead is subordinate, and the chief metal is silver. The minerals are quartz, tetrahedrite, argentiferous galena, with small amounts of sphalerite, ruby silver, chalcopyrite, pyrite, pyrrhotite, calcite, and siderite. . . . The ores in the roof sediments near the contact are less siliceous, contain more galena, sphalerite, siderite, and calcite, with less tetrahedrite and ruby silver, and about the same proportions of pyrite and chalcopyrite. In the more distant deposits the relative proportions of galena and sphalerite to quartz is greater, and siderite and calcite are more abundant while chalcopyrite and pyrite remain about the same. Tetrahedrite and ruby silver are still present, but the proportion of these minerals with respect to the amount of galena and sphalerite is much less than in the ores in the granodiorite.

In many respects this zoning in the Slocan district is very similar to that in the Hyder district, but differs radically in the fact that galena in the latter area decreases relatively, outward from the source.

Hypogene Deposition.—The vast bulk of the ore minerals in the veins in the Salmon River section of the Hyder district were deposited from ascending magmatic solutions. The relations, as seen in the field and under the microscope, are those that have

[11] Bateman, A. M., *op. cit.*, p. 563.

come to be regarded as characteristic of undoubted hypogene deposits. The ore minerals, practically without exception, reveal smooth contacts with one another. Where later minerals have replaced earlier ones, the feathery and concentric structures, so characteristic of veinlets resulting from supergene alteration, are not present, with the exception of unimportant alterations in surface outcrops to be discussed later.

The hypogene ore minerals of the veins are pyrite, galena, chalcopyrite, sphalerite, pyrrhotite, arsenopyrite, molybdenite, chalmersite, gold, and five minerals which could not be identified because of their minute size.

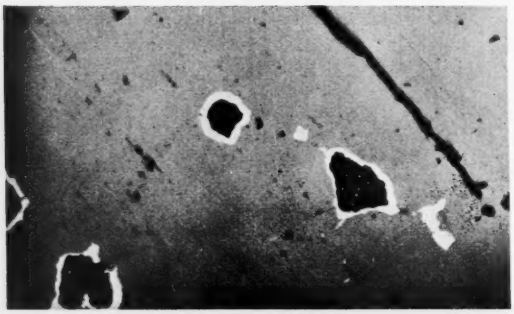

FIG. 1. Rings of chalcopyrite around sphalerite. The groundmass is tetrahedrite. × 251.

By far the most common minerals are pyrite, galena, sphalerite, and chalcopyrite. Almost any polished section of the heavily mineralized portions of the veins reveals these four sulphides. Pyrrhotite and arsenopyrite, though very common, occur chiefly in the roof rocks. Pyrite is probably the most abundant sulphide present, and is the earliest abundant mineral to form. Where occurring with other sulphides, it is generally brecciated and corroded or in isolated cubes showing only faint corrosion. Pyrrhotite, where present with pyrite or arsenopyrite, is later, as shown by its veining relations towards them.

Chalcopyrite is as widely distributed as any other sulphide. It is, however, by no means the most abundant. It generally occurs intimately associated with the sphalerite in the typical so-called emulsion or microlamellar structures or as irregular areas replacing the sphalerite. A peculiar relation of chalcopyrite to sphalerite is shown in Fig. 1. The explanation is not apparent. It is generally earlier than galena, but occasionally is contemporaneous with it. Sphalerite, though distributed almost as widely as pyrite, chalcopyrite, and galena, is not very abundant in the veins within the granodiorite. It is generally nearly always present in these veins, but usually makes up but a small part of the sulphides. The veins in the country rock, however, often contain shoots of

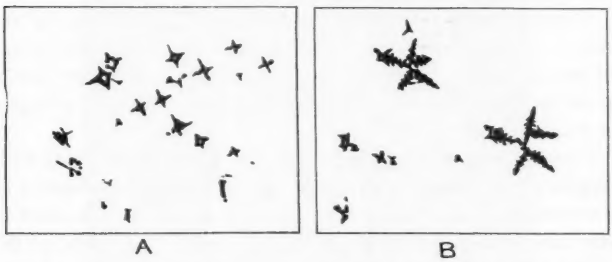

FIG. 2. *A*. Stars of sphalerite (skeleton crystals?) in chalcopyrite. ×360. *B*. Stars of sphalerite (skeleton crystals?) in chalcopyrite. ×300.

solid sulphides in which sphalerite is by far the most abundant mineral. The sphalerite varies greatly in color from almost black to yellowish brown and buff colored varieties. The lighter colored varieties rarely contain much chalcopyrite, and when present it never occurs as emulsion or lamellar structures. The darker varieties of sphalerite, on the other hand, almost always contain rounded blebs and spikes of chalcopyrite oriented in regular patterns. In the polished sections from two veins, peculiar star-shaped grains of sphalerite (Fig. 2) occur thickly clustered in the vicinity of residual grains of sphalerite in chalcopyrite. Most of

these stars have four arms, some have five, and some fewer. In one section they are extremely regular in size and shape, and occasionally contain minute blebs of chalcopyrite. The fact that they occur clustered in the vicinity of residual grains of sphalerite in the chalcopyrite would seem to suggest that they represent remnants of sphalerite which have been replaced differentially along the cleavage by chalcopyrite. The extreme regularity, however, of the stars, both as regards shape and size, makes their origin by replacement very doubtful. Similar stars have been found by Hugh McKinstry [12] in material from Ivigtut, Greenland, and by Emmons and Laney [13] in chalcopyrite at Ducktown, Tenn. As suggested by Emmons and Laney, they have the characters of skeleton crystals.

Tetrahedrite is widespread, occurring in 38 per cent. of the veins. It is generally observed as small irregular blebs and grains of microscopic size in galena. Occasionally tetrahedrite occurs, as on the Fish Creek and Homestake properties, in solid stringers up to a few inches wide.

Freibergite is relatively rare. In the few veins in which freibergite was observed it was always associated with tetrahedrite as scattered microscopic blebs in galena. Molybdenite was noted in only one instance. It occurs as flakes facing seams in one of the aplite dikes that extend for short distances from the Texas-Hazelton contact. Chalmersite, regarded as a rare mineral up to a few years ago, is now known to be quite widely distributed. It was observed in but one vein in this district, where it occurs as long blade-like laths in chalcopyrite, but not in pyrrhotite, though the latter mineral is abundant in the same polished section. Recent experiments by Schwartz [14] seem to indicate that chalmersite (cubanite) is not formed below 400° C.

Gold occurs on several properties in the district, generally as

[12] Personal communication from W. H. Newhouse.

[13] Emmons, W. H., and Laney, F. B., "Geology and Ore Deposits of the Ducktown Mining District, Tenn.," U. S. Geol. Surv. Prof. Paper 139, p. 47, Pls. XXXVII.–XLII.

[14] Schwartz, G. M., "Intergrowths of Chalcopyrite and Cubanite," ECON. GEOL., vol. 22, pp. 44–61, 1927.

flakes facing small joints and slips. Gold was seen in a polished section from the Silver King Group as small irregular grains in tetrahedrite. It has been reported in the adjoining Canadian territory by both McConnell [15] and Dolmage.[16] Burton [17] attributes most of the gold values in the Premier ore to the presence of electrum. This alloy of gold and silver was not observed in any of the 250 polished sections studied by the writer. The tungsten mineral, scheelite, was noted in but four of the veins. In two of them, however, it was relatively abundant. Barite generally occurs with scheelite and invariably veins and replaces it and the quartz associated with it.

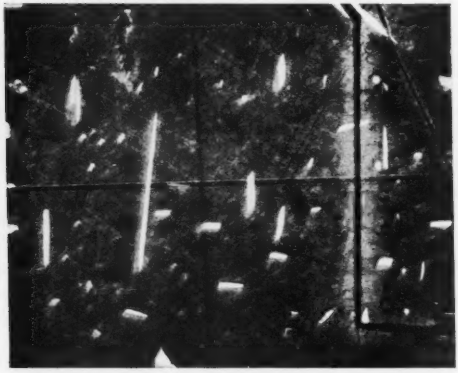

FIG. 3. Unknown mineral (No. 1) spikes in galena. Galena etched with HCl. × 103.

Five minerals were distinguished in the ores that could not be positively identified. In their mode of occurrence they may easily be mistaken for tetrahedrite or argentite. They occur as microscopic blebs, grains, and spikes associated with galena and tetra-

[15] McConnell, R. G., "Portland Canal District," Can. Geol. Survey Summary Report for 1910, pp. 59–89.

[16] Dolmage, Victor, *Can. Min. Journal*, vol. 41, pp. 454–458, 1920.

[17] Burton, W. D., "Ore Deposition at Premier Mine, B. C.," ECON. GEOL., vol. 21, pp. 586–604, 1926.

hedrite. All of them show sharp mutual boundaries with the galena and tetrahedrite. Some of these unknowns were observed in ores from the Porter-Idaho and Independence properties on the Canadian side. With one exception, all of these undetermined minerals differ from any mineral described by Davy and

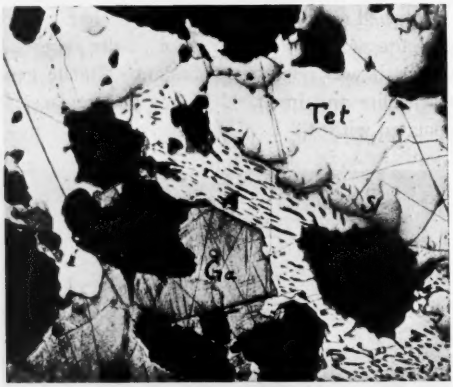

FIG. 4. Intergrowth of unknown minerals (No. 2). Intergrowth is localized between tetrahedrite (Tet) and galena (Ga). Galena and galena-white part of intergrowth etched with HCl. Sphalerite (Sl) occurs as residual grains in the tetrahedrite. Black areas are solution pits in the calcite gangue. × 110.

Farnham [18] or by Murdoch.[19] The exception, a bright white mineral, resembles one described by Murdoch [20] from Bisbee, Arizona, and labeled by him "unknown." The remaining undetermined minerals are described in the footnote below.[21]

[18] Davy, W. M., and Farnham, C. M., "Microscopic Examination of the Ore Minerals," McGraw-Hill Book Co., 1920.

[19] Murdoch, J., "Microscopic Determination of the Opaque Minerals," John Wiley & Sons, 1916.

[20] Murdoch, J., *op. cit.*, p. 130.

[21] (1) A strongly anisotropic mineral occurring as rounded blebs and spikes with typical emulsion structures in galena (Fig. 3). Color—grayish white; pleochroism —in one position the mineral is a perfect color match for galena, and in the other

It is strongly suspected from the similarity of both physical properties and microchemical reactions that all the unknowns may be sulphosalts of copper or lead or both with perhaps some silver.

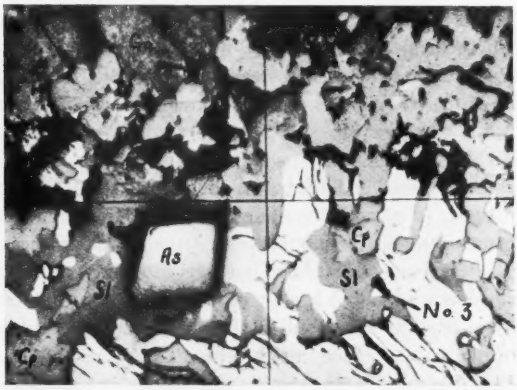

FIG. 5. Strongly anisotropic unknown mineral (No. 3) associated with chalcopyrite (Cp), galena—etched with HCl (Ga), sphalerite (Sl), and arsenopyrite (As). × 180.

position can hardly be distinguished from tetrahedrite in color; hardness—same as galena; x nicols—strongly anisotropic, though showing no color; etch tests—same as for tetrahedrite.

(2) A typical graphic intergrowth, both parts of which are distinctly anisotropic (Fig. 4). One part of the intergrowth is grayish white (between tetrahedrite and galena in color), while the other portion is the exact duplicate of galena in color, the intergrowth seems to occur exclusively along tetrahedrite-galena contacts. Etch tests for the grayish white part of the intergrowth were as follows: HNO_3—neg.; HCl—neg.; KCN—very slowly faint brown; $FeCl_3$—neg.; $HgCl_2$—tarnishes dark brown, rubs almost clean; KOH—neg. Etch tests for the galena-white part of the intergrowth gave: HNO_3—like galena; HCl—like galena; KCN—neg.; $FeCl_3$—neg.; $HgCl_2$—tarnishes dark brown, rubs almost clean; KOH—neg.

(3) A strongly anisotropic mineral, generally occurring as irregular grains or blades of microscopic size in galena (Fig. 5). It is often associated with the graphic intergrowth. Color—practically same as galena but sometimes slightly grayish; hardness—about that of galena; x nicols—strongly anisotropic giving pale browns and blues; HNO_3—tarnishes dark like galena but more slowly; HCl—neg.; KCN—neg.; $FeCl_3$—neg.; $HgCl_2$—neg.; KOH—neg.

(4) A pale bluish white mineral somewhat resembling ruby silver in color. It

In connection with efforts to determine these unknown minerals, several specimens of argentite, known to have the composition of Ag_2S, from the Premier mine in British Columbia, Lake Valley, N. M., Montezuma, Colorado, and Freiberg, Saxony, were studied. Each of these specimens was found to give the appropriate microchemical reactions assigned to argentite, but to be distinctly anisotropic under crossed nicols. Both twinning and grain structure were observed, the latter being more common. Ag_2S [22] at low temperatures has been referred to the orthorhombic system, which would explain its anisotropic character.

Supergene Deposition.—Supergene alteration in the veins in the Hyder district is scant and confined to surface outcrops and persistent fractures. It is unimportant, from an economic standpoint, in the veins examined. That it is more important on the Canadian side is advanced by Burton,[23] who believes that some of the rich sulpho-salts and veinlets of native silver in the Premier ores are due to supergene enrichment. Dolmage, on the other hand, though admitting that some supergene enrichment may have taken place, leads one to believe that he, at least, believes the Premier ores to be almost exclusively primary. He says:[24]

> The small amount of stephanite ore to be found in the district, the comparatively low grade character of the silicious ore, and the great preponderance of primary over secondary minerals in all the ore except the stephanite ore, indicate that the processes of secondary enrichment may have played only a very subordinate rôle, if any, in the formation of these rich silver deposits.

That supergene enrichment has occurred in this region was impressed upon the writer in a visit to the Porter-Idaho mine in the adjacent area of British Columbia. The upper workings of this mine (at one place to a depth of at least 200 feet below the out-

occurs associated with tetrahedrite in galena as microscopic grains and blebs. Hardness—about that of galena; x nicols—faintly anisotropic showing a grain structure; HNO_3—neg.; HCl—neg.; KCN—tarnishes quickly iridescent to black; $FeCl_3$—nearly always neg.; $HgCl_2$—practically neg.; KOH—neg.

[22] Emmons, R. C., Stockwell, C. H., and Jones, R. H. B., "Argentite and Acanthite," *Am. Mineralogist*, pp. 326–329, 1926.

[23] Burton, W. D., *op. cit.*, p. 598.

[24] Dolmage, Victor, *op. cit.*, p. 457.

crop) are in ore that has been intensely altered by surface waters. The ore consists of yellowish to brownish-colored "dirt" that contains abundant wire silver, and is reported to carry up to 2,000 ounces of silver to the ton. The veins at the Porter-Idaho are unique in the district, so far as the writer's experience goes. The entire Salmon River district has been exposed to erosion since the beginning of the Tertiary, at least, and it might be expected that important supergene alterations had taken place. The region has been intensively glaciated, however, during the Pleistocene and subsequently. Mountain glaciers may even have existed in this section of the Coast Range in the late Tertiary. Enormous quantities of material have been swept away by the glaciers, and the rock exposed by recent retreats of the present ice tongues is fresh without exception. It is probable, therefore, that only relics of pre-glacial and interglacial secondary enrichment are preserved, and that unimportant amounts of supergene alteration were accomplished during post-glacial time.

The minerals that have resulted from this brief weathering are limonite, marcasite, anglesite, covellite, malachite, azurite, and possibly proustite and calcite. Feathery and concentric structures are common in veinlets of limonite crossing other minerals. Marcasite occurs almost exclusively as an alteration product of pyrrhotite and is clearly, in all but one case, the result of surface alteration. It occurs in irregular veinlets with concentric structures (Fig. 6) and as feathery aggregates in the pyrrhotite. Anglesite is a common alteration product of galena and often occurs in remarkably regular lattice patterns. The veinlets of anglesite almost always follow the cleavage of the galena, and occasionally expand into irregular areas.

Covellite occurs as typical supergene veinlets through both tetrahedrite and chalcopyrite. Infrequently the covellite has replaced the chalcopyrite in irregular masses. Ruby silver was identified in but one of the veins, though it has been reported from a few other properties. It occurs filling small fractures in the galena and gangue, and is thought to be supergene. A study of more specimens is desirable to make this conclusive. The bril-

liant blood-red color under crossed nicols, together with its slight difference in reaction with reagents, make it seem probable that this ruby silver is proustite and not pyrargyrite, which is locally abundant in the Premier ores.

FIG. 6. Concentric supergene marcasite replacing pyrrhotite. × 116.

Gangue Minerals.—The gangue minerals of the veins are principally quartz, calcite, and barite, with small amounts of ankerite. Sericite is abundant in the wall rocks, but is rare or absent in the veins themselves. The quartz, for the most part, is white and milky, in sharp contrast to the vitreous quartz in the veins related to the later quartz monzonites and granodiorites of the Coast Range batholith. Burton [25] reports adularia in abundance at the Premier mine. No trace of adularia was observed in the 87 veins studied in detail on the American side. Barite, though only locally abundant, occurs in a considerable number of the deposits and must be considered a common gangue mineral. It shows a marked concentration in the veins within the Texas batholith. Where barite occurs in considerable quantities, tetrahedrite is also more abundant. Calcite is a common and locally abundant gangue

[25] Burton, W. D., *op. cit.*, p. 596.

mineral in the deposits of the district. This is true of the deposits in the roof rocks, though calcite is almost entirely absent from the deposits within the granodiorite. It is often coarsely crystalline, and may occur in solid stringers up to several inches wide. Calcite shows a marked association with pyrrhotite, being present in varying amounts in nearly every deposit where the latter is abundant. Probably some of the calcite, at least, was deposited by supergene solutions, but no data are available to suggest how important this is quantitatively. Ankerite is present locally in small amounts in a few of the veins, but is very rare. Siderite is reported as being fairly common in the adjacent Canadian area.

Classification.—Westgate [26] has called these deposits intermediate in type, while Burton [27] apparently considers the Premier deposit shallow seated, comparing it to the deposits at Tonopah, Nevada. The mineralization and paragenesis show no change in the deposits related to the Texas granodiorite through a vertical range of over 5,000 feet. In order that similar mineralization could take place in two deposits that are nearly a mile apart vertically, it may be assumed that a cover of 5,000 feet or probably more capped the higher veins at the time of their deposition. This would make the lower veins formed at a depth of 10,000 feet or more.

These deposits are Jurassic or, at the most, Lower Cretaceous in age; and since there is no evidence of subsidence below sea level since that time in the area, there has been an immensely long time during which erosion has been active. It is therefore probable that great thicknesses of rock have been removed, and surely any shallow seated deposit would have disappeared. Galena, sphalerite, and tetrahedrite are generally considered to belong principally to the intermediate type of vein. Sphalerite, however, is often found in contact metamorphic deposits, and has even been reported as a primary constituent of a granite.[28] Pyrite and chalcopyrite are also persistent minerals. Galena and tetrahedrite, espe-

[26] Westgate, L. G., *op. cit.*, p. 130.

[27] Burton, W. D., *op. cit.*, p. 601.

[28] Rimann, E., "Magmatische Ausscheidung von Zincblende in Granit," *Zeitsch. f. prakt. Geol.*, vol. 18, pp. 123–124, 1910.

cially the former, are probably more characteristic of the intermediate veins; yet they are both late in the order of deposition in the veins in the Hyder district.

The presence of considerable arsenopyrite and pyrrhotite, together with the presence of scheelite, when considered with the other evidence, seems sufficient to show that the veins are not wholly intermediate in the usual sense of the term, and certainly not low temperature or shallow seated types. They are not, on the other hand, typical high temperature veins, as are those related to the main Coast Range intrusives in the district. They are in part composite veins that contain considerable quantities of high temperature minerals, associated with those characteristic of intermediate temperature. In general, they carry a fairly large percentage of minerals that are characteristic of the intermediate zone, with the preponderance of the minerals suggesting conditions on the border line between the intermediate and deep vein zones. They may then, perhaps, be called deep-intermediate veins.

Paragenesis.—The order of deposition of the various hypogene ore minerals is the same in all the veins studied, irrespective of their position relative to the Texas-Hazelton contact, altitude, or type of country rock. Occasional reversals occur, but they are always in cases where the minerals concerned were deposited very nearly together, and some overlapping might therefore be expected. The order given below is that present in the great majority of the veins:

1. Scheelite.
2. Pyrite and arsenopyrite.
3. Arsenopyrite.
4. Pyrrhotite.
5. Sphalerite, chalmersite, and chalcopyrite.
6. Chalcopyrite.
7. Chalcopyrite, galena, tetrahedrite, freibergite, gold (?), and undetermined minerals.
8. Tetrahedrite, freibergite, undetermined minerals.

Similarity to Adjacent Canadian Deposits.—The deposits under discussion and those in the adjacent territory of British Columbia resemble one another to a considerable degree. The writer has arrived at this conclusion, both from a study of 30 polished sections from five Canadian properties, and from the descriptions of Dolmage,[29] Schofield and Hanson,[30] McConnell,[31] and Burton.[32] The Canadian deposits differ locally in their content of native silver and rich silver minerals. The latter are only locally abundant, however; and the great bulk of the Canadian deposits, even at the Premier mine, are similar in all respects to those in the Hyder district. This close similarity between the deposits on either side of the International Boundary is not surprising, for they were formed at the same time geologically, show marked relationships to the same host rocks, and have a common origin.

Genesis.—The fact that the deposits in the Hyder district occur almost wholly within 1,500 feet of the Texas granodiorite-Hazelton Group contact suggests strongly that the solutions from which the ores were deposited were derived from the cooling Texas magma. The fissure veins well within the batholith are proof that much of the outer shell of the granodiorite had already solidified at the time of intensive metallization. Fractures through this crust and the overlying sediments and volcanics became channels through which solutions from below escaped; and as they migrated outward from the source, presumably pockets in the still unconsolidated or only partially crystallized magma below, lower temperatures and pressures, or other changes of environment were encountered, which resulted in the precipitation of their mineral content. Where persistent fractures did not exist in the weaker members of the roof rocks, deposits resulted chiefly from replacement of the country rock by the ascending solutions along bedding planes or in the mashed material lying in and near shear zones. The disseminated deposits in the greenstones were precipitated from solutions and vapors which saturated and soaked these relatively permeable rocks.

[29] Dolmage, Victor, *loc. cit.*

[30] Schofield, S. J., and Hanson, George, *loc. cit.*

[31] McConnell, R. G., *loc. cit.*

[32] Burton, W. D., *loc. cit.*

The Texas granodiorite is different in many respects from that which forms such a large portion of the Coast Range intrusives. These later granodiorites were essentially wet, as shown by the vast amount of pegmatite associated with them. On the western border of the great batholith, pegmatite dikes, stringers, and segregations occur in great profusion, and along the Chickamin River such evidences of high water content in the granodiorite magma occur almost continuously for a distance of twenty miles from the mouth of the river. Metamorphism of the intruded rocks has also proceeded to a considerable degree, resulting in reaction and injection gneisses, schists, and the development of typical contact minerals. The Texas granodiorite, on the other hand, has practically no pegmatite dikes associated with it, while aplite dikes usually extend less than 500 feet from the contact. Where it has intruded the rocks of the Hazelton Group, the sediments and volcanics are wholly unaltered to within a few inches of the actual contact.

TABLE III.

COMPARISON OF THE TEXAS GRANODIORITE WITH THE GRANODIORITES OF THE MAIN COAST RANGE BATHOLITH.

	(1)	(2)
Andesine	48	44
Potassic feldspar	20	21.6
Quartz	19	20
Hornblende	10	6
Biotite	2.5	7
Accessories	0.5	1.4

(1) Average of 22 Rosiwal analyses of the Texas granodiorite.

(2) Average of 44 Rosiwal analyses of the core of the Coast Range batholith between Portland Canal and the Stikine River.[33]

These two granodiorites so different in their effects upon the country rocks, are very similar in mineral composition, as is shown in Table III. Both are the average of a large number of analyses, and may therefore be taken as fairly representative. Both have almost identical amounts of quartz, andesine, potassic

[33] The writer is indebted to A. F. Buddington for the analyses of the granodiorites along Portland Canal and the Stikine River.

feldspar, and combined hornblende and biotite. The hornblende and biotite when considered separately, however, show a striking difference. Hornblende is four times as abundant as biotite in the Texas, while biotite is in excess of hornblende in the granodiorites of the main batholith.

This marked difference in the hornblende-biotite ratios, the absence of pegmatite dikes, schistosity, and contact minerals in the country rock, and the primary gneissic structure in the Texas batholith, suggest strongly that the original magma that froze into the Texas granodiorite was relatively dry . . . at least much drier than that of the main Coast Range batholith.

The solutions that gave rise to the deposits may have been relatively dry. It is thought possible that this dryness is responsible for the peculiar zoning exhibited by the deposits and for the deposition of typically intermediate minerals so many thousands of feet below the actual surface. In relatively dry solutions, such as the ones postulated as responsible for the deposits, slight changes in temperature and pressure might cause saturation and precipitation. Minerals that would have been carried much farther toward the surface under ordinary conditions were deposited relatively close to their source.

The mineralization accompanying and closely following the intrusion of the quartz monzonite and related rocks of the main Coast Range batholith was slight in the area, and of a wholly different type from the earlier one. A number of veins are found consisting of glassy quartz with pyrite, magnetite, and specularite. The pyrite is veined and replaced by magnetite and specularite. Magnetite, where it is associated with specularite, replaces the latter. This is shown by the bladed habit of the magnetite, which is pseudomorphous after the specularite. Occasionally feathery specularite of a second generation replaces this bladed magnetite. Similar relations between magnetite and specularite have been observed by Burbank [34] in a study of the ore deposits of the Republic of Haiti, and by Gilbert [35] and others.

[34] Woodring, W. P., Brown, J. S., and Burbank, W. S., "Geology of the Republic of Haiti," Republic of Haiti, Dept. of Public Works, 1924, p. 438.

[35] Gilbert, G., "Some Magnetite-Hematite Relations," ECON. GEOL., p. 590, 1925.

SUMMARY.

The ore deposits of the Hyder district are chiefly fissure veins mineralized principally with pyrite, galena, sphalerite, and chalcopyrite in a quartz gangue. Replacement deposits occur in the roof rocks as disseminations and as partial replacements of brecciated country rock in shatter and shear zones. The country rock has been extensively altered to quartz, sericite, chlorite, and carbonate. A peculiar zoning is present in which pyrite, galena, chalcopyrite, tetrahedrite-freibergite, quartz, and barite show a tendency to occur in the genetically associated intrusive, and pyrrhotite, arsenopyrite, sphalerite, and calcite in the roof rocks. Hypogene minerals make up the vast bulk of the ore and consist of pyrite, galena, sphalerite, chalcopyrite, tetrahedrite, pyrrhotite, arsenopyrite, freibergite, scheelite, gold, chalmersite, molybdenite, and five minerals that the writer was unable to identify.

Supergene ore minerals are sparse or absent. They were probably formed during post-glacial time, and are of no economic importance. They include limonite, marcasite, anglesite, covellite, malachite, azurite, and perhaps proustite. The gangue minerals consist principally of quartz, with locally abundant calcite and barite and small amounts of ankerite.

Some of the veins of the district were deposited at depths of probably more than 10,000 feet. They are composite veins containing both high temperature and intermediate minerals which were all deposited during the same period of mineralization. The bulk of the deposits were precipitated under high temperature-intermediate conditions, and may be classified as of high temperature-intermediate or deep-intermediate type. It is believed that the relative dryness of the parent magma is partly or wholly responsible for this telescoping. The order of deposition of the hypogene ore minerals is the same in all the veins studied, irrespective of their position relative to the Texas-Hazelton Group contact, elevation, or type of country rock. The following order is that present in the great majority of the veins: scheelite; pyrite and arsenopyrite; arsenopyrite; pyrrhotite; sphalerite, chalmersite, and chalcopyrite; chalcopyrite; chalcopyrite, galena, tetrahedrite,

gold (?), freibergite, and undetermined minerals; tetrahedrite, freibergite, and undetermined minerals.

With the exception of their locally abundant content of native silver and sulpho-salts of silver, the deposits in the adjacent territory of British Columbia are remarkably similar to the deposits in the Hyder district. It is believed that both were formed at the same time and have a common origin.

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EDITORIAL

EXPLOITATION OF FOREIGN MINERALS.

To the geologist it is almost axiomatic that mineral resources are very irregularly distributed among the nations of the globe; that no nation has adequate supplies of all necessary minerals; that some nations are deficient in most of the essential ones; that others have excess supplies which must be used by other countries. A balanced ration of minerals essential for modern industry must be drawn from many parts of the globe. This fact is becoming increasingly apparent with the vastly enlarging requirements of modern industry. As the demand multiplies it tends to converge more and more on the few really large sources of supply, wherever they may be.

It is an obvious fact also that the driving power in exploration, development, extraction, and shipment of the world's mineral resources has its principal origin in the great industrial centers which are largely grouped in the countries about the North Atlantic basin. Political barriers of one kind or another often offer resistance, but adjustments are ultimately made and the international movement of minerals goes on. Other countries in most cases do not have the necessary capital, or experience, or organizing power.

Inherent in this situation is the necessity for *exploitation* of foreign minerals. The primary meaning of the word "exploit" is to develop, or get the value out of, but there has come to be attached to it the idea of unfairness, selfishness, and force, which is now reflected in supplementary definitions in dictionaries. In the public mind the objectionable connotations so over-shadow the primary meaning that the term has come to stand for one of the most undesirable of human activities. I use the term here mainly in its primary sense, but not exclusively so. If a less provocative term like "develop" were substituted, it would probably

not be understood by most people as covering essentially the same activity which has come historically to be known as exploitation. The term should identify the facts, whether they are regarded as good or bad. Even the best of *development* is not always free from selfishness and unfairness; the worst of *exploitation* is seldom without some underlying justification in world needs.

Governments have seldom been frank about foreign exploitation. They often deny it or hide it behind a general phrase like "defense of national interests." The public statements of our officials in regard to the recent Mexican and Nicaraguan difficulties are cases in point. A large section of the public criticizes all exploitation *per se* and assumes that it can be and should be stopped. Neither attitude has any considerable effect on the actual progress of exploitation—it continues inexorably in response to demand. It is rather a common assumption that both demand and exploitation might be curbed by political measures, yet the very people taking this position go right on buying household utilities and automobiles which create the demand, without realizing that they are just as responsible as any one else for demand and thus for exploitation.

In the turmoil of political discussion of this problem the atmosphere would be greatly cleared by the common recognition of the simple fact that exploitation is an inevitable consequence of nature's irregular distribution of resources and of our habits of living; that in all probability it will continue with accelerating pace, whatever we may think or do about it; that it is no more right or wrong than nature's original creation of inequalities in mineral environment. At best it results in a certain amount of interference with other nations' internal affairs, an over-riding of national self-determination, and is in fact a phase of economic imperialism. The United States is and must continue to be one of the world's chief exploiters.

If this could be understood, it would clear the ground for a much more profitable attack on the problem, that is, as to the *manner* of exploitation and the correction of its abuses. There are great opportunities for the improvement of procedure with

the view to compromise the legitimate national aspirations with the equally insistent world pressure. Many recent specific bargains between nations and commercial companies seem to point the way to a better formulation of international agreements touching this important subject. It involves a clear understanding of the principles underlying the "open" and "closed" political doors, of the rôle of tariffs, and of the many other political barriers which are causes of international friction.

Economic geologists should be in a better position than any one else to help the public to realize that mineral exploitation is not a mere bit of human deviltry but essentially a product of environment, and their wide experience on the firing line of exploitation should qualify them to offer constructive suggestions for its improvement.

C. K. LEITH.

DISCUSSION AND INFORMAL COMMUNICATIONS

A PHYSICO-CHEMICAL THEORY OF METASOMATISM.

Sir: In number 8 of volume 21, H. C. Boydell gives his opinion on the physical chemistry of metasomatism in response to my remarks in number 1 of volume 21 (p. 91).

Mr. Boydell mentions that the heading of my answer was changed to "Metasomatic Processes in Fissure Veins." The correct title, "Metasomatic Processes in Silicate Rocks," was given on the cover page of number 1 of volume 21, but an unfortunate typographical error brought about an exchange of the last two words of the title on page 91.[1]

Concerning the reality of the question discussed I regret to state that Mr. Boydell's answer does not convince me of the soundness of his view. Mr. Boydell compares the physico-chemistry of metasomatism with any case of double decomposition with the formation of a solid product and claims that the formation of a solid product in such a case is dependent on the concentration of two components, not on the concentration of one component.

I think that Mr. Boydell seems unaware of the fact that metasomatism means the transformation of a solid mineral (or several solid minerals) to another solid mineral (or minerals) by means of solutions (or gaseous phases) under such conditions that the products are formed in the presence of the educts. There is more than one solid phase present and therefore the variability of the liquid phase is restricted, as the reacting masses (the concentration in the solution or the vapor-pressure in the gaseous phase) of the educt-minerals and of the product-minerals are determined by their solubilities (or vapor-tensions).

[1] The Editor regrets that this typographical error was overlooked in his office.

Mr. Boydell quotes as an example the following reaction:

$$H_2SO_4 + \underset{\text{solid}}{CaO} = \underset{\text{solid}}{CaSO_4} + H_2O$$

the formation of calcium-sulphate by metasomatic replacement of CaO. He states concerning the amounts of substances involved, that the amount of water would be so greatly in excess that the addition of one mole of water makes no appreciable difference.

It would appear, that Mr. Boydell is unaware of the fact that the reaction will give another solid product quite neglected by Mr. Boydell, and that product is solid $Ca(OH)_2$. There will not occur in physico-chemical equilibrium the solid phases CaO and $CaSO_4$ in contact with a solution containing much excess water, but there will be the solid phases $Ca(OH)_2$ and $CaSO_4$.

The formation of solid $CaSO_4$ will be dependent only on the concentration of H_2SO_4 in the invading solution, as the phase $Ca(OH)_2$ will be present in the solid state and the concentration of the calcium will be given by the solubility of that mineral.

The same statement will hold, if instead of regarding only undissociated H_2SO_4, $CaSO_4$ etc., we take into consideration the ionization and hydrolysis of the different molecules in solution. These processes are of importance if we deduct the numerical value of the critical minimum concentration, but they do not affect the general statement made by me, that every case of mineral replacement demands the presence of a definite minimum concentration of the active (added) substance in the invading fluid.

If at least this minimum concentration is present, then the mineral replacement will be produced; if the concentration of the active substance (in the case quoted the H_2SO_4) is less than that minimum, no mineral replacement will result however prolonged may be the presence of the invading solution and however great may be the total amount of solution passing through the rock.

It is just the difference between metasomatism (mineral replacement) and other processes of mineral formation (as crystallization from ordinary solutions or from magmas), that the range

of concentration of the liquid (or gaseous) phase is restricted by the presence of more than one mineral partaking in the reaction. This restriction of the variability of the liquid phase makes the difference between the physical chemistry of metasomatism and the physico-chemistry of other processes of mineral formation.

I hope that this explanation, perhaps somewhat elementary, may be sufficient to prove the correctness of my statement.

V. M. GOLDSCHMIDT.

MINERALOGICAL INSTITUTE OF THE UNIVERSITY,
OSLO, NORWAY.

EXPLORING AND REPAIRING LEAKY ARTESIAN WELLS.

A recently issued press bulletin of the Department of the Interior, U. S. Geological Survey, states that: In some of the first wells drilled in the Dakota artesian basin the pressure of the water at the top of the wells was more than 150 pounds to the square inch, and the well at Woonsocket, S. Dak., was reported to have a pressure of 250 pounds to the square inch. Some artesian wells deliver immense quantities of water by natural pressure. For example, the Tinderry bore, in Australia, at first flowed 2,520 gallons a minute; a well near San Bernardino, Calif., flowed 3,730 gallons; a well at Chamberlain, S. Dak., flowed 4,350 gallons; and a well near Roswell, N. Mex., flowed 5,710 gallons. The flow of the well near Roswell amounted, in other terms, to about 13 cubic feet a second, or eight million gallons a day. For many years it has been surmised that large quantities of artesian water are lost by leaking underground through holes in the corroded casings of the artesian wells. Recently the U. S. Geological Survey has developed a practical method of locating these leaks and measuring the quantities of water that are wasted through them.

The method is simple in principle. A current meter that was specially constructed for the purpose by Carl H. Au, of the Geological Survey, is let down into the well, where it records the velocity of the water at any depth desired. With the velocity and

the diameter of the well known, the rate of flow at any point can be determined. Hence a series of measurements taken at successive levels from the bottom to the top of the well will show just where the water enters and in what amounts, where it leaks out and in what amounts, and how much is delivered at the surface. For certain investigations it may be necessary to devise apparatus for measuring the diameter of a well at any depth, but thus far no serious difficulties have arisen on account of uncertainty as to the diameter.

This method has now been successfully used in the artesian area of Honolulu, and in the Roswell artesian basin, in the Pecos Valley of New Mexico. In Honolulu the artesian water is especially valuable, because it forms the principal supply for the city. In nineteen defective wells in Honolulu a total underground leakage of 7,750,000 gallons a day was found, which is equal to about one third of the total quantity of artesian water consumed from the public waterworks. One of the wells was found to waste 750,000 gallons a day by underground leakage. A somewhat expensive program of recasing or plugging all leaky artesian wells has been undertaken, and the value of the work already completed is indicated by the fact that leakage amounting to 5,900,000 gallons a day has been effectively stopped. The experience on this project has shown that recasing and plugging leaky wells are expensive and difficult operations, which require the services of a skillful driller with adequate equipment, working under the instructions of a competent hydraulic engineer. The methods are described in more detail in reports by John McCombs and A. G. Fiedler, which have been published by the Geological Survey as Water-Supply Paper 596-A.

DOCTORS IN GEOLOGY AND GEOGRAPHY IN 1927.

The following list of men and women receiving doctor's degrees in Geology and Geography from American universities in 1927 embraces approximately the output of young geographers and geologists whose special training has been carried to the doctorate stage, with designation of the seat of their final training, and such indication of their special interest and professional preparation as may be found in the subjects of their doctor theses. The compilation has been made in the Division of Geology and Geography of the National Research Council in order to establish records of those receiving advanced university preparation for work in our branches of the earth's science. It is felt, however, that the opportunity to review the vintage of 1927 in this brief form will be welcomed by professional geographers and geologists.

Due to the relatively early date of the canvass, the list is subject to errors, chiefly of omission. The writer seizes the occasion heartily to thank his colleagues in the different universities for their cordial cooperation and generally prompt transmission of the requested data.

DAVID WHITE, Chairman,
Division of Geology and Geography,
NATIONAL RESEARCH COUNCIL,
Washington, D. C.

June 30, 1927.

DOCTORS IN GEOLOGY AND GEOGRAPHY IN 1927.

Name of Student	*University granting Doctor's degree*	*Subject of Doctor's thesis*
1. Adler, Joseph Leopold	Chicago	Geology of a Portion of the Front Range in the Region West of Denver, Colorado.
2. Bain, George William	Columbia	Geology and Problems of the Webbwood Area, Canada.
3. Ball, John Rice	Chicago	The Faunas of the Brassfield and Bainbridge Limestones of Southeastern Missouri.

Name of Student	*University granting Doctor's degree*	*Subject of Doctor's thesis*
4. Bannerman, Harold MacColl	Princeton	The Iron Ranges of Nickel Lake and Furlonge Lake, Rainy River District, Ontario.
5. Bengston, Nels August.	Clark *	Studies in the Geography of Honduras.
6. Billings, M. P.	Harvard	The Geology of North Conway Quadrangle.
7. Bradley, W. H.	Yale	The Origin and Microfossils of the Green River Formation of Colorado and Utah.
8. Brown, Robert Wesley.	Chicago	Folds of the Osage Type.
9. Buffam, Basil Scott Whyte	Princeton	Geology of the Palmarolle and O'Brien Map Areas, Quebec.
10. Chambers, William Trout	Chicago *	A Geographic Study of Joliet, Illinois, an Urban Center Dominated by Manufacturing.
11. Chen, H. H.	Harvard	Problem of Genesis of Certain Secondary Vanadates, Molybdates and Associated Minerals.
12. Cooper, Clyde Edwards.	Clark *	Luzon—The Island and Its People.
13. Coulter, John Wesley	Chicago *	The Geography of the Santa Lucia Mountain Region.
14. Dodge, Stanley Dalton.	Chicago *	Bureau and the Princeton Community.
15. Ekblaw, George E.	Stanford	Clastic Deposits in Playas.
16. Evans, Charles Sparling.	Princeton	Geology of Brisco-Bogtooth Map Area, British Columbia.
17. Grawe, O. R.	Iowa State	A Study of the Carbonaceous Shales in the Cromwell Oil Field, Oklahoma.

Name of Student	*University granting Doctor's degree*	*Subject of Doctor's thesis*
18. Gray, Anton	Minnesota	Ore Deposits of the Mineral Hill District, Idaho.
19. Greig, J. W.	Harvard	The Immiscibility in Silicate Melts.
20. Gwynne, C. S.	Cornell	Weathering of pre-Cambrian Rocks in Central Wisconsin.
21. Hall, Robert Burnett	Michigan *	The Geography of the Republic of Haiti, a Study in the Structure and Evolution of Landscape.
22. Hansen, George H.	George Washington	The Cretaceous of South Central New Mexico and Adjoining Regions.
23. Harvey, R. D.	Harvard	Use of Electrical Conductivity and the Dielectric Constants for Determination of Opaque Minerals in Polished Section.
24. Holzwasser, Florrie	Columbia	Geology of Newburgh and Vicinity.
25. Knappen, Russell Stafford	Columbia	Geology and Mineral Resources of the Dixon Quadrangle, Illinois.
26. Knechtel, Maxwell M.	Johns Hopkins	The Cretaceous Ammonites of the Ellsworth Expedition to Northern Peru.
27. Leighly, John Barger	California *	A Study in Urban Morphology: the Towns of Malärdalen in Sweden.
28. Link, Theodore August.	Chicago	Three Dimensional Experiments in Earth Deformation.
29. Lugn, Alvin L.	Iowa State	A Study of the Sedimentation of the Mississippi River from Davenport, Iowa, to Cairo, Illinois.

Name of Student	*University granting Doctor's degree*	*Subject of Doctor's thesis*
30. Lusk, R. G.	Harvard	The Geology and Oil and Gas Resources of the Gainesboro Quadrangle, Tennessee.
31. Mansfield, Wendell C.	George Washington	The Miocene Stratigraphy of Virginia, Based upon the Study of the Faunas.
32. Morse, W. C.	Mass. Inst. Technology	Paleozoic Rocks of Mississippi.
33. Mortimore, M. M.	Iowa State	Correlation of oil sands and Sedimentary Analysis.
34. Moss, Frank Ambrose	California	The Geology of the Mother Lode in the Vicinity of Carson Hill, Calaveras County, California.
35. Muilenburg, Garrett A.	Columbia	Geology of the Tarryall District, Park County, Colorado.
36. Pegrum, Reginald Herbert	Princeton	The Nephelite Syenites of the French River Region, Ontario.
37. Perry, Elwyn Lionel	Princeton	The Geology of Plymouth and Bridgewater Townships, Vermont.
38. Polspoel, Lambert Gaston	Chicago*	The Trade in Pork and Pork Products from the United States to Northwest Europe.
39. Poor, Russell Spurgeon	Illinois	Stratigraphic and Sedimentation Studies in the Galesburg Quadrangle.
40. Renner, George Thomas, Jr.	Columbia	Primitive Religion in Tropical Forests.
41. Richards, Gragg	Clark*	The Rainfall of Florida.

Name of Student	*University granting Doctor's degree*	*Subject of Doctor's thesis*
42. Russell, W. L.	Yale	Structure, Stratigraphy and Economic Geology of a Portion of the Black Hills Region, South Dakota.
43. Smith, G. H.	Wisconsin *	Geographical Factors in the Distribution of Population in Wisconsin.
44. Squires, Henry Dayton.	Wisconsin	Areal and Structural Geology of the St. George Map Area.
45. Stainbrook, M. A.	Iowa State	Brachiopods of the Cedar Valley.
46. Stark, John Thomas.	Chicago	The Geology of the Kekequabic Lake Area, Northeastern Minnesota.
47. Sutton, Arle Herbert.	Chicago	Geology of the Dawson Springs Quadrangle, Kentucky.
48. Tolman, C. F.	Yale	Geology and Correlation of the Killarney Granites, Ontario, Canada.
49. Touwaide, Marcel E.	Stanford	Genesis of the Boleo Copper Deposits.
50. Vanderwilt, J. W.	Harvard	I. The Nature of Polishing; Abrasion instead of "Amorphous-Flow." II. Improvements in the polishing of Ores.
51. Weller, James Marwin.	Chicago	Geology of Edmonson County, Kentucky.
52. Whitbeck, Florence.	Wisconsin *	A Geographical Interpretation of Porto Rico.
53. Wood, Ella Lucille.	Wisconsin *	A History of the Modern Concept of Geography.

* Indicates separate Departments of Geography.

REVIEWS

Laterit, Material und Versuch erdgeschichtlicher Auswertung. By HERMANN HARRASSOWITZ, Ph.D., Professor of Geology and Paleontology and Director of the Geological and Paleontological Institutes of the University of Giessen. Pp. 314. Price 24 marks. Borntraeger Brothers, Berlin, 1926.

"Laterite, the basis for interpretation of earth history," is a free English rendition of the title of this paper, a volume containing much information of value to geology particularly to metamorphic geology. Likewise, it is of interest to students of ore deposits, since certain important classes of metalliferous deposits, such as the bauxite deposits of Arkansas, the nickel deposits of New Caledonia, and the lateritic iron ores of Cuba, have undoubtedly originated in this manner.

The major portion of the volume is given over to a description of recent and fossil laterite formations, with many excellent sketches and a great number of chemical analyses—most of which are original. This part of the work constitutes in itself a complete chemical study of laterite sections, or profiles, as the author designates them, and is believed to be the first such ever published. However, the description of laterites is not the main purpose of the study but is made the basis for certain deductions concerning past climatic conditions in various parts of the earth, particularly during Carboniferous and Tertiary times. Further, the opening discussion is not concerned with laterite, but with the origin of superficial beds of kaolinite and their association with coal.

Kaolinite is discussed in great detail. Two new words are coined: "siallite" (Si + Al + lithos), to designate those hydrous aluminum silicate formations originating through the decomposition of older rocks, and "allite," for those which consist essentially of aluminum hydrates. Kaolinite and allophanite are given as the principal siallites, while bauxite and laterite are the chief allites. A new method of interpreting analyses to show important chemical changes in decomposition processes is introduced and applied. The genetic significance of stratigraphic relations and composition of beds is discussed. A review of the literature on the genesis of siallite, including a long list of references on kaolinite, and the general opinion regarding the cause of decomposition by swamp waters are given. The chapter concludes with a discussion of the apparent connection between the genesis of siallite and overlying coal beds.

Bleached or acid soils—"podsol" decomposition, as it is termed by the author—is next considered. Because of similar light coloration, such formations are commonly confused with kaolinite. An extended discussion of laterite is then taken up; general description of laterite sections, the mineral contents, the chemistry of formation, differing development of sections, and the climatic conditions necessary for its production follow in order. The lateritic character of Central European kaolinite and its later alteration are discussed, also the occurrence of free aluminum hydrates and the appearance of lateritic sections, particularly the reduced sections beneath lignite in Bohemia and a similar degradation of bauxite beds under coal. The geological occurrence of free alumina is dealt with briefly.

Fossil laterites of the Tertiary, Cretaceous, and Carboniferous periods in different countries are fully described, illustrated and discussed in the next hundred pages. The laterite of the Vogelsbergs in Germany is considered in special detail. Isolated occurrences in Jurassic, Triassic and Permian formations are mentioned. The relationship between laterite and coal is then taken up. The very frequent occurrence of laterite beds beneath coal beds is pointed out, also that both are common products of similar climates and that their genesis jointly depends on endogenous processes. Finally, climatic questions relative to Carboniferous and Tertiary times are considered. Evidence for the past prevalence of various types of climate is discussed and deductions made.

An appendix contains late references and analyses.

This volume by Dr. Harrassowitz is of especial value in the study of metamorphic processes, particularly katamorphism by laterization. The many clear descriptions and drawings, the numerous group analyses, and the able discussion given to the whole make it a veritable mine of useful information.

R. J. LEONARD.

UNIVERSITY OF ARIZONA,
TUCSON, ARIZ.

The Geology and Metal Deposits of Chile. By JAMES M. LITTLE, E.M. 188 pages, 12 plates, 14 figs. 2 maps in pocket. The Bramwell Company, New York, 1926.

The author states in the preface that the material contained in this book was gathered during two and one half years spent in the examination of mines in Chile and, except for statistics of production, was obtained directly from field observation. The book then represents the author's own work and no references are given to any literature.

The first chapter deals with general geology. No great amount of de-

tail can be expected and one cannot but admire the author for unraveling as many of the complexities as he has, but one also wishes that he had been more careful in the choice of terms and in his classification. For instance the terms "Intrusive Eruptive Rocks" in the table of contents and again on page 11 followed by "Plutonic Eruptive Rocks" on the same page are rather puzzling. In the table of rock formations on page 4 the oldest formation under "Secondary Age, Stratified Rocks" is "Diorite Porphyry." The text explains that this rock generally underlies the sedimentary rocks and "in some occurrences it is bedded and obviously extrusive," but the terms are incongruous. In the same table "Red Sandstone" is used as a formation name to include such divers rock types as limestone, quartzite, tuff, igneous extrusives and intrusives, as well as sandstone. Admittedly the sandstone predominates but a better group name could have been chosen.

Chapter II. covers the field of the ore deposits. They are classified genetically as well as according to the periods of deposition, temperature of mineralizing solutions, and form. The age, distribution, mineralogic composition, structural features, and oxidation and enrichment of the ores; the magmatic source of the mineralizing solutions and the factors that caused the differential precipitation of minerals are all considered. Here again, however, the classifications are somewhat jumbled. As one example, on page 60 the reader is confronted by the heading "Classification of Epigenetic Deposits according to form." This jumps from veins and irregular mineralized breccias to replacement and contact metamorphic deposits. It is as though one should classify automobiles by saying that some are long and low, others are made by hand. Other similar illogical and poor usages occur.

Chapter III. contains a description of all the mines and includes a valuable table giving the mine, metal, district, nature of the deposit, country rock, primary sulphides, gangue and temperature of deposition.

Chapter IV. deals with the production of metals in Chile, the principal copper producing districts and the resources of Chile in the various metals.

There is a great deal of valuable information contained between the covers of this book and the reviewer believes that it merited a more careful presentation. The errors mentioned above, a certain amount of careless phrasing and the unpleasing physical make up of the book itself prejudice the reader against much of the more valuable descriptive part.

WILLIAM M. AGAR.

YALE UNIVERSITY,
NEW HAVEN, CONN.

Geology of South Africa. By ALEX. L. DU TOIT. 444 pp., index, 39 plates, 64 figures and geological map. Oliver & Boyd, Edinburgh, 1926. Price, 28 shillings.

This is a textbook of South African geology. Chapter I. treats of Geologic Principles, Chapter II. is an outline of Physical Geography and Geology. In Chapters III. to XVII. the different geological systems from "Primitive" to "Recent" are described carefully and in detail. The mineral products associated with them are considered briefly and the fauna are described and pictured. Also the interesting tillites receive attention and are illustrated by excellent photographs. The next four chapters deal with "Primitive Man," "Soils of South Africa," "Economic Geology," and the "Geological History of South Africa." An appendix contains tables of rock analysis. The chapter on Economic Geology describes briefly the occurrence and character of the important deposits of each metal. The gold banket and diamond deposits are treated more fully under the systems in the main body of the book.

The book is written by one who is a master of the subject. The author brings together the experience of years of field work and careful study, and the discrimination of the trained geologist is evident in the compilation of that part which is not personal observation. It is a book that should be in every geological library, and one that will be constantly referred to by those interested in geological problems of the African continent. It is also a handy reference to many interesting ore deposits of South Africa. The publisher has produced a finely printed, well illustrated and substantially bound book.

ALAN BATEMAN.

Geology of Alabama. By GEORGE I. ADAMS, CHARLES BUTTS, L. W. STEPHENSON, AND WYTHE COOK. Special Rept. No. 14, Geol. Survey Alabama, 312 pages, 97 plates, 1926.

This report, with its accompanying geologic map, is one of the very best and most detailed of its kind ever printed, and is a great honor to all concerned. The Paleozoic formations are described in great detail and with a wealth of illustrations of guide fossils by Butts (pp. 41–230, and 24 paleogeographic maps). Stephenson handles the Cretaceous (pp. 231–245), and Cook the Cenozoic (251–297). The guide fossils for all the formations are illustrated in the best manner, with 45 plates for the Paleozoic, 7 for the Mesozoic, and 5 for the Cenozoic. In addition, there are many illustrations of outcrops. The crystalline rocks are treated by Adams (pp. 25–40).

This splendid treatise is recommended to all teachers of postgraduate students in stratigraphy as collateral reading to illustrate the lectures and

laboratory work, and, further, as an example of how areal geology should be done.

CHARLES SCHUCHERT.

Soil and Civilization. By MILTON WHITNEY. 278 pp. Index. D. Van Nostrand Co., New York, 1925. Price, $3.00.

This is another of the Library of Modern Science series, written in popular style by the chief of the Bureau of Soils of the U. S. Department of Agriculture. It is, therefore, authoritative. It is not a technical book, but it does give a concept of the soil as a living thing and a producer of living things. Chapter I. describes the soils of the different geographic provinces of the United States, Chapter II., methods of soil culture, Chapter III., the "Rôle of Fertilizers," acquaints the reader with the use of fertilizers by the ancients and its development of today. But perhaps the most interesting parts are Chapters V. and VI., which tell of the "Development of Man" through the agriculture in the older communities of the world. A bit of history and the trend of a science are linked together.

It is readable and interesting, and he who peruses its pages will appreciate more fully the relation of agriculture to the development of countries. It is well printed and nicely bound in blue cloth.

ALAN BATEMAN.

Kleine Geologische Karte von Europa and **Tektonisches Bild von Europa.** By E. BEYSCHLAG and W. SCHRIEB. Issued under the auspices of the Prussian Geological Survey by Gebrüder Borntraeger, Berlin.

It appears to be desirable to call the attention of geologists to this excellent little geologic map of Europe in which the general distribution of the rocks of the principal geologic divisions is effectively displayed on a sheet that is only about 2 feet by 2.5 feet in size. Accompanying the map is a chart to the same scale, on transparent paper, on which are shown the principal structural elements with the designations as applied to them by Prof. Stille of Göttingen. The pre-Cambrian shields, the mountain systems of the successive geologic periods, the great *massifs*, the areas of subsidence, and the important structural basins are all clearly shown and named.

The price of the unmounted map, with its overprint, is 15 marks.

F. L. RANSOME.

SCIENTIFIC NOTES AND NEWS

Percy E. Barbour left this country on June 22 for a six weeks' trip in Spain, France, and other European countries.

Guy C. Riddell returned to New York recently after spending three months with an exploring party, aided by army airplanes, in examining and photographing mining concessions and water power sites in Panama.

L. C. Graton, professor of mining geology at Harvard University, has left for fifteen months in Europe, South America, Africa and India, to study, with the aid of grants from the Bureau of International Research and the Shaler Memorial Fund, the geological and operating conditions in the world's deepest mines, and examine the great copper deposits of South America and Africa.

W. J. Mead, who has been giving courses in structural and metamorphic geology at the University of California during the past year, gave a series of six lectures in metamorphic geology at Stanford University in May. He has lately been examining power sites in North Carolina and Tennessee, and will resume work at the University of Wisconsin in the fall.

F. L. Ransome recently examined the quicksilver properties of the Tonto Mining Company and the Arizona Cinnabar Company in the Mazatzal Mountains, Arizona. He is also to make a thorough study of the geology of the United Verde Extension Mining Company mine at Jerome, Arizona.

N. H. Darton has been spending six months in exploring the geology of a part of central Venezuela.

E. Kaiser, professor of geology in the University of Munich, is spending several months in South Africa, and will tour through Southwest Africa and the Kalahari.

H. W. Turner of San Francisco, Cal., spent July in mine examination work in Montana.

J. J. O'Neill, of McGill University, Montreal, Canada, is to spend the summer in geological work in western Canada for the Mond Nickel Company and the Victoria Syndicate.

W. L. Russell has gone to Venezuela for the Gulf Oil Company.

H. D. Smith has returned from a professional visit to South America.

G. A. Clothier, mining engineer for the Northwestern district, British Columbia, has been transferred to the Nanaimo district, succeeding W. M. Brewer, retired.

Norman B. Davis has resigned his position with M. J. O'Brien Limited, to take up private practice as consulting mining geologist at 410 Blackburn Building, Ottawa, Canada.

J. A. Bancroft, formerly professor of geology in McGill University, Montreal, Canada, has joined the technical staff at Broken Hill, South Africa, as consulting geologist for the Anglo-American Corporation.

Arthur Keith and W. S. Bayley have returned from a ten days' trip through the marble district in Georgia.

Donald C. Barton has severed his connection with the magnetometric and gravimetric section of the Geophysical Research Corporation except as consultant, and has opened an office as consulting geologist and geophysicist at 717 Petroleum Building, Houston, Texas.

Douglas G. H. Wright, former chief geologist and field engineer for Domes Mines Limited, has opened an office as consulting mining engineer and geologist at 906 Royal Bank Building, Toronto, Canada.

Charles F. Rand, past president of the American Institute of Mining and Metallurgical Engineers, died on June 21, at his home in West Orange, N. J., at the age of seventy.

Among the projects undertaken by the Topographic and Geologic Survey of Pennsylvania for the present field season are the following: G. H. Ashley, popular report on the Rocks of Pennsylvania; R. W. Stone, field work on building stones; J. D. Sisler, reconnaissance of oil and gas fields; Anna I. Jonas, in coöperation with George W. Stose of the U. S. Geological Survey, areal mapping, Middletown and York quadrangles; Herbert Hughes, areal mapping, Freeport quadrangle; Frank Leverett, of the U. S. Geological Survey, study of glacial geology; George H. Chadwick, stratigraphic study in the oil and gas region of northwestern Pennsylvania; Henry Leighton, studies of the Pittsburgh district clay deposits; Freeman Ward, Lafayette College, areal studies of sand and gravel deposits; Charles H. Behre, Jr., studies of slate west of Lehigh River; Arthur M. Piper, underground water resources of northwestern Pennsylvania.

On May 7, a fire at the Pennsylvania State printery destroyed nearly all the stock of Survey bulletins. It is hoped, however, that the more recent ones may be reprinted.